

**Isolated *cyclo*-Tetraarsendiide Anions:  
Synthesis and Crystal Structures  
of Bis(tetraamminelithium) tetraarsenide  
[Li(NH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>As<sub>4</sub>, Bis(pentaamminesodium)  
tetraarsenide – ammonia (1/3)  
[Na(NH<sub>3</sub>)<sub>5</sub>]<sub>2</sub>As<sub>4</sub> · 3NH<sub>3</sub> and Bis[(4,7,13,  
16,21,24-hexaoxa-1,10-diazabicyclo  
[8.8.8]hexacosan)(cesium, rubidium)]  
tetraarsenide – ammonia (1/2)  
[Cs<sub>0.35</sub>Rb<sub>0.65</sub>(2,2,2-*crypt*)]<sub>2</sub>As<sub>4</sub> · 2NH<sub>3</sub>**

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**Summary.** The ammoniates [Li(NH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>As<sub>4</sub>, [Na(NH<sub>3</sub>)<sub>5</sub>]<sub>2</sub>As<sub>4</sub> · 3NH<sub>3</sub>, and [Cs<sub>0.35</sub>Rb<sub>0.65</sub>(2,2,2-*crypt*)]<sub>2</sub>As<sub>4</sub> · 2NH<sub>3</sub> (2,2,2-*crypt*: 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosan) were synthesised either by direct reduction of arsenic with Li(Ca)/Na in liquid ammonia or by reaction of Rb<sub>4</sub>As<sub>6</sub> with CsPH<sub>2</sub> in the same solvent. Single crystals were isolated and characterised by low temperature X-ray structure analysis. All three compounds contain As<sub>4</sub><sup>2-</sup> anions of almost square planar geometry which have no contacts to metal ions. The medium As–As bond length in the putatively aromatic anions is 2.362 Å.

**Keywords.** Ammoniates; Arsenic; Crystal structure; Liquid ammonia.

## Introduction

Among the polyanions of group 15 elements, polyarsenide anions have been less intensively investigated than the corresponding polyphosphide species. Neverthe-

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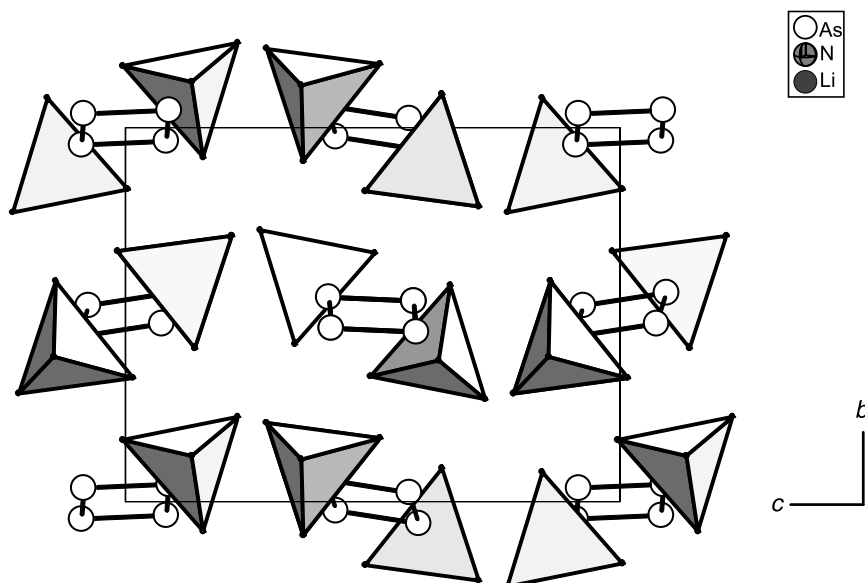
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less, a number of different molecular anions have been reported so far, which occur with alkali metal or alkaline earth metal counter ions in binary compounds or in structures with typical alkali metal ion ligands like cryptands, crown ethers, or other ethers. In the 1930s, *Zintl* and co-workers published electrochemical studies of sodium-arsenic alloys, where the compound  $\text{Na}_3\text{As}_7$  was mentioned [1]. Analogous compounds with cage-structured anions like  $\text{As}_7^{3-}$  and  $\text{As}_{11}^{3-}$  may be the best-known polyarsenides, as they can be synthesised by classical high temperature reactions from the elements as well as from precursors in organic solvents or by various reactions in liquid ammonia [2–11].  $\text{Na}_4\text{Ba}_3\text{As}_6$  and  $\text{K}_5\text{As}_4$  are examples for compounds with finite-chain polyarsenide anions [12, 13]. Whereas  $\text{Na}_4\text{Ba}_3\text{As}_6$  contains the normal, electron-precise  $\text{As}_3^{5-}$  anion, the situation in  $\text{K}_5\text{As}_4$  is more complicated, as the anionic part of the structure can be best described as a *catena-As* $_4^{4-}$  anion and an extra delocalised electron, which implies a certain degree of arsenic–arsenic multiple bonding. Planar cyclic polyarsenide anions are  $\text{As}_4^{4-}$ ,  $\text{As}_6^{4-}$ , and  $\text{As}_4^{2-}$ . The first can be found in the skutterudite-type structure of  $\text{CoAs}_3$  [14], but very strong cobalt-arsenic interactions make an ionic interpretation of this compound and a comparison to other arsenides difficult.  $\text{As}_6^{4-}$  occurs in  $\text{Rb}_4\text{As}_6$  and  $\text{Cs}_4\text{As}_6$ , which were obtained by classical high temperature reactions from the elements [15]. Formally, the  $\text{As}_6^{4-}$  ion has one arsenic–arsenic double bond, which is delocalised in the isometric ring. The putatively aromatic  $\text{As}_4^{2-}$  anion in the compound  $[\text{Na}(\text{NH}_3)_5]_2\text{As}_4 \cdot 3\text{NH}_3$  was synthesised in our group by direct reduction of arsenic with sodium in liquid ammonia [16]. Liquid ammonia is a good solvent for alkali metal polyarsenides. However, ammonia molecules tend to be incorporated into the compounds crystallizing from these solutions, resulting in ammoniates like  $\text{Cs}_3\text{As}_7 \cdot \text{NH}_3$  [17] and  $[\text{Na}(\text{NH}_3)_5]_2\text{As}_4 \cdot 3\text{NH}_3$  [16]. The former is one of the rare examples of room temperature-stable ammoniates, the majority of ammonia-containing solvate crystals like  $[\text{Li}(\text{NH}_3)_4]_3\text{As}_7 \cdot \text{NH}_3$  or  $\text{Cs}_3\text{As}_7 \cdot 6\text{NH}_3$  [18] are thermally unstable above approximately  $-10^\circ\text{C}$ . Using low temperature crystallographic techniques, the structural characterisation of such unstable ammoniates is possible nowadays. In this contribution, three ammoniate compounds containing the  $\text{As}_4^{2-}$  anion are presented, which were encountered during our work with elemental arsenic and alkali metal arsenides in liquid ammonia.

## Results and Discussion

The ammoniate compounds  $[\text{Li}(\text{NH}_3)_4]_2\text{As}_4$  (**1**),  $[\text{Na}(\text{NH}_3)_5]_2\text{As}_4 \cdot 3\text{NH}_3$  (**2**), and  $[\text{Cs}_{0.35}\text{Rb}_{0.65}(2,2,2\text{-crypt})]_2\text{As}_4 \cdot 2\text{NH}_3$  (**3**) were prepared by different routes. Direct reduction of the grey elemental modification of arsenic in liquid ammonia with sodium resulted in the formation of **2**. Compound **1** was obtained of an ammonia solution of grey elemental arsenic, elemental aluminum, and both lithium and calcium metal as reducing agents. The reaction of  $\text{Rb}_4\text{As}_6$  with  $\text{CsPH}_2$  in liquid ammonia yielded compound **3**. All three compounds contain the planar *cyclo-As* $_4^{2-}$  ion.

The crystal structure of compound **1** is built of discrete tetraarsenide anions and approximately tetrahedral  $[\text{Li}(\text{NH}_3)_4]^+$  cations (Fig. 1).

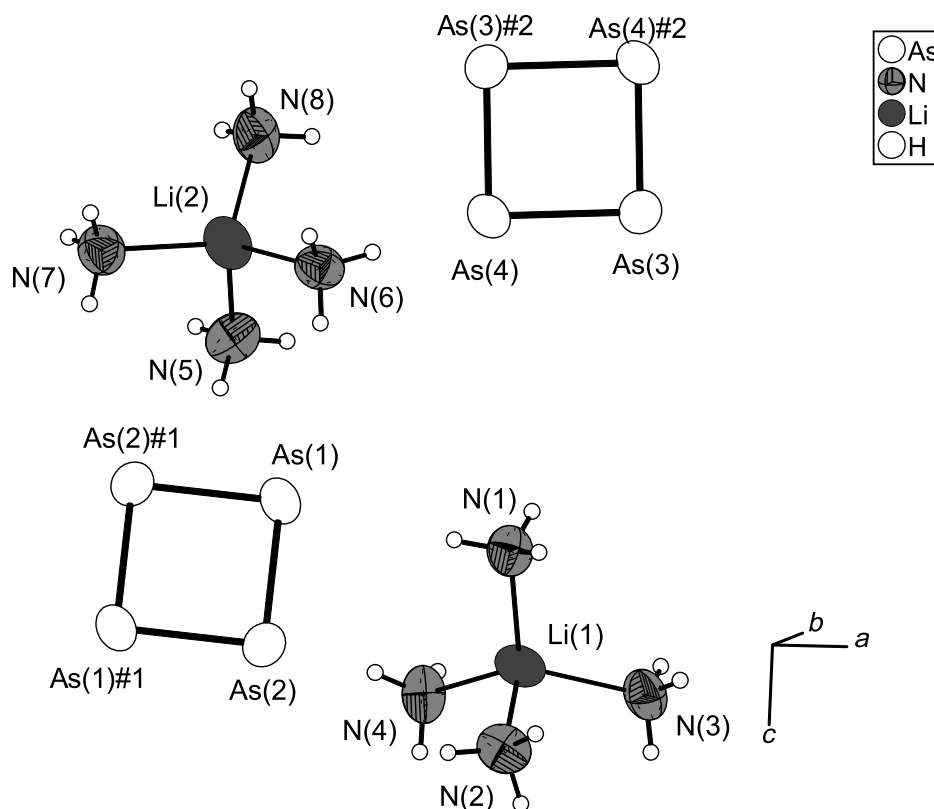


**Fig. 1.** Projection of the unit cell contents of  $[\text{Li}(\text{NH}_3)_4]_2\text{As}_4$  on the  $bc$ -plane showing the lithium-tetraamine complexes in polyhedral design; hydrogen atoms are omitted for clarity

The centres of the two crystallographically independent anions lie on the special positions  $2d$  and  $2a$  of space group  $P2_1/c$ . Consequently, only four independent arsenic atoms build up the two *cyclo*-tetraarsendiide anions. The As–As bond distances of 2.356(1) and 2.360(1) Å as well as the angles of 90.14(5) and 90.43(5)° and of 2.361(1) and 2.363(1) Å, and 89.57(5) and 89.86(5)° show only minimal deviations from an ideal square. Due to the symmetry constraints, the anions are perfectly planar. The Li–N bond distances in both of the crystallographically independent tetraamminelithium cations lie between 2.04(2) and 2.08(2) Å and the N–Li–N angles differ by a maximum of 10.5° from the ideal tetrahedron angle (Fig. 2).

The crystal structure of compound **2** consists of pentaamminesodium complexes,  $\text{As}_4^{2-}$  rings, and additional ammonia molecules of crystallisation (Fig. 3).

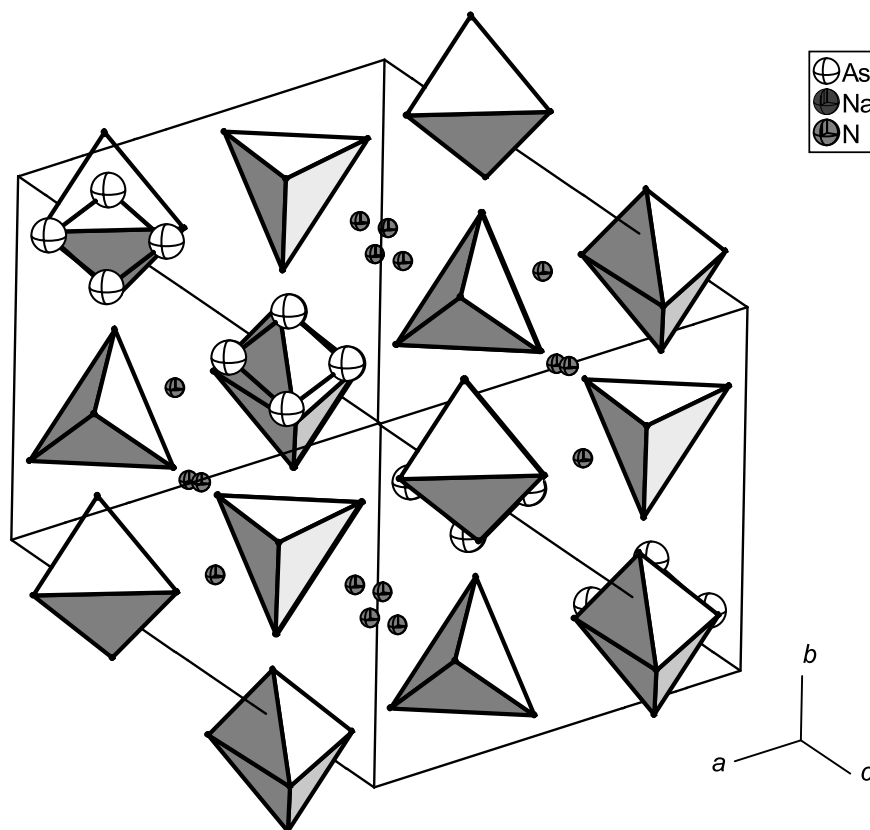
In this structure, the tetraarsendiide anions are situated on the crystallographic two-fold rotation axis of the space group  $I2/a$  with As(1) and As(3) occupying the special positions  $4e$ . Thus, only two independent As–As bond length (2.3439(8) and 2.3453(8) Å) and three independent angles (90.47(4), 89.57(2), and 90.40(4)°) are observed. The  $[\text{Na}(\text{NH}_3)_5]^+$  complexes are of trigonal bipyramidal shape with Na–N distances of 2.443(4) to 2.592(4) Å and N–Na–N angles of 129.6(2) to 111.5(2)° and 82.8(2) to 95.9(2)°, respectively. Three ammonia molecules of crystallisation complete the structure. Hydrogen bonds (see Fig. 4) between the ammonia molecules of crystallisation and the pentaamminesodium complexes lead to the formation of layers parallel to the  $ab$ -plane with the  $\text{As}_4^{2-}$  anions situated between these layers. The N···N distances in these hydrogen bonds lie between 3.07(1) and 3.38(1) Å, which corresponds to N···H distances of 2.03(4) to 2.66 Å and means



**Fig. 2.** Detail of the structure of  $[\text{Li}(\text{NH}_3)_4]_2\text{As}_4$ ; ellipsoids are drawn with a probability factor of 70%; hydrogen atoms are omitted for clarity; distances (in Å) and angles (in °): As(1)–As(2) 2.356(1), As(1)–As(2)#1 2.360(1), As(3)–As(4) 2.361(1), As(3)–As(4)#2 2.363(1), Li(1)–N(1) 2.04(2), Li(1)–N(4) 2.07(2), Li(1)–N(3) 2.08(2), Li(1)–N(2) 2.08(2), Li(2)–N(8) 2.05(2), Li(2)–N(5) 2.06(2), Li(2)–N(6) 2.07(2), Li(2)–N(7) 2.08(2); As(2)–As(1)–As(2)#1 90.43(5), As(1)–As(2)–As(1)#1 89.57(5), As(4)–As(3)–As(4)#2 89.86(5), As(3)–As(4)–As(3)#2 90.14(5), N(1)–Li(1)–N(4) 114.8(9), N(1)–Li(1)–N(3) 111.6(8), N(4)–Li(1)–N(3) 119.6(9), N(1)–Li(1)–N(2) 102.9(8), N(4)–Li(1)–N(2) 105.7(8), N(3)–Li(1)–N(2) 99.2(8), N(8)–Li(2)–N(5) 104.9(8), N(8)–Li(2)–N(6) 110.4(8), N(5)–Li(2)–N(6) 108.0(9), N(8)–Li(2)–N(7) 113.1(9), N(5)–Li(2)–N(7) 99.6(8), N(6)–Li(2)–N(7) 119.2(9); symmetry operations: #1 =  $-x + 1, -y, -z + 1$ ; #2 =  $-x + 2, -y, -z$

shortenings relatively to the *van der Waals* radii (H: 1.20 Å, N: 1.55 Å) of 3.3 to 26.2%. The angles differ from ideal linearity by a minimum of 15° and by a maximum of 43° (Fig. 4).

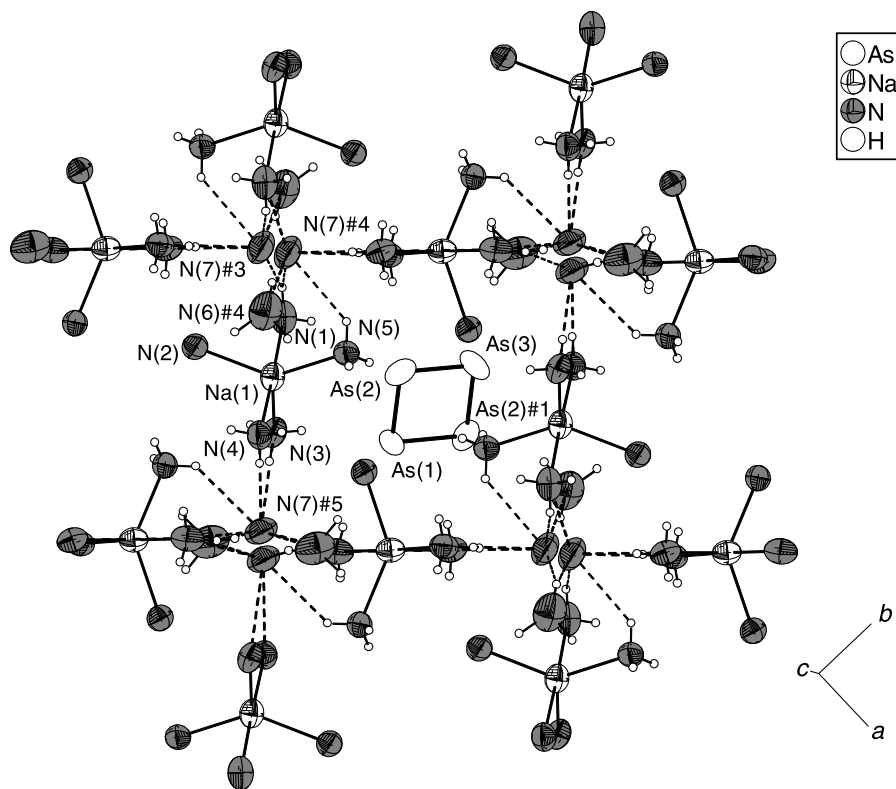
Compound **3** crystallises in the triclinic space group  $P\bar{1}$ . The centres of the two independent  $\text{As}_4^{2-}$  anions lie on the special positions 1g and 1a, respectively. The As–As bond distances in the tetraarsendiide anions lie between 2.3797(8) and 2.3857(8) Å, and the angles between 89.69(3) and 90.31(3)°. The two cationic sites are occupied by approximately 35% cesium and 65% rubidium, both of which are enclosed in molecules of 2,2,2-*crypt*. Refinement of the data without this mixed occupation as either the pure rubidium or cesium compound resulted in significantly worse agreement factors. We were unable to find a similar example of mixed occupation of 2,2,2-*crypt* in the literature (Fig. 5).



**Fig. 3.** Projection of the unit cell contents of  $[\text{Na}(\text{NH}_3)_5]_2\text{As}_4 \cdot 3\text{NH}_3$  along  $(-1-1-1)$  showing the pentaamminesodium complexes in polyhedral design; hydrogen atoms are omitted for clarity

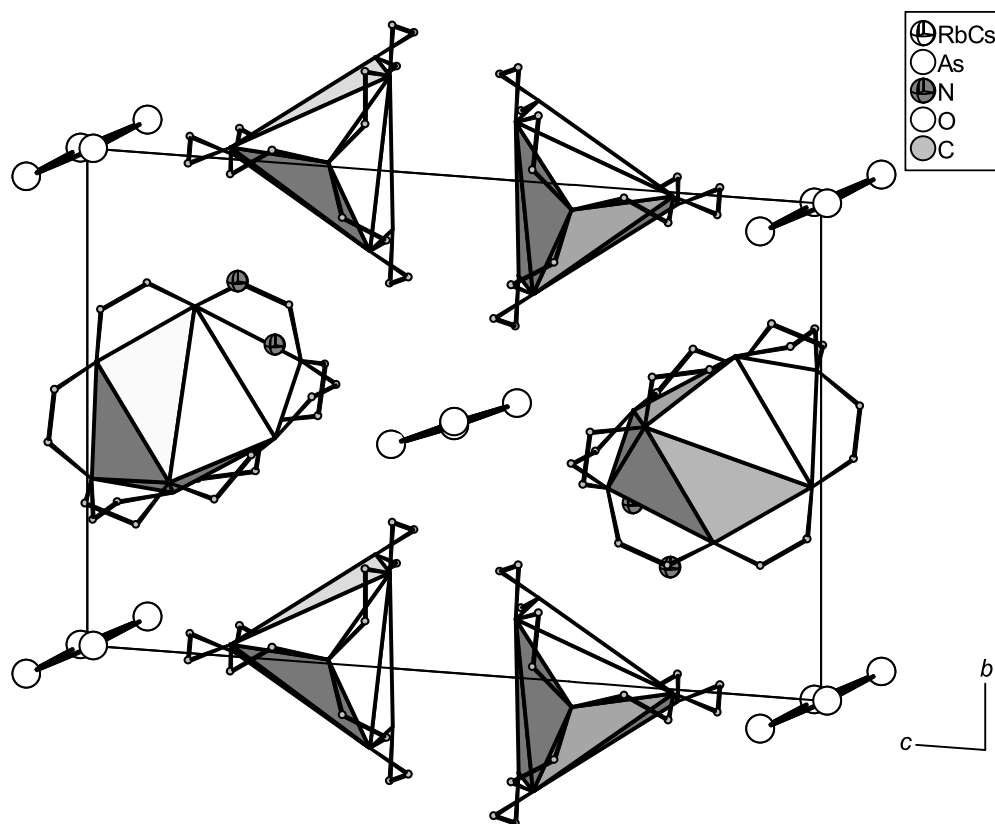
Two ammonia molecules of crystallisation form hydrogen bonds between each other and to oxygen atoms connecting two neighboured cryptand molecules (see Fig. 6). The distances are 3.347(8) Å for  $\text{N} \cdots \text{N}$  (2.49(7) Å for  $\text{N} \cdots \text{H}$ , shortening 9.5%) and 3.221(7) to 3.424(7) Å for  $\text{N} \cdots \text{O}$ , which corresponds to  $\text{O} \cdots \text{H}$  distances of 2.38(7) to 2.57(8) Å and means shortenings relatively to the *van der Waals* radii (H: 1.20 Å, O: 1.52 Å) of 5.5 to 12.5% (Fig. 6).

In compounds **1–3**, there are no contacts between the  $\text{As}_4^{2-}$  anions and the corresponding alkali metal cations. Compounds **1** and **2** contain the non-coordinating homoleptic ammine complexes  $[\text{Li}(\text{NH}_3)_4]^+$  and  $[\text{Na}(\text{NH}_3)_5]^+$ , whereas the  $\text{Cs}^+/\text{Rb}^+$  cations in **3** are enclosed in 2,2,2-*crypt* ligands and are therefore protected from contacts to the anion as well. The lithiumtetraammine cations in **1** are typical for lithium containing ammoniates [18–21], which may be explained by the well-known HSAB principle [22]. The harder acid  $\text{Li}^+$  is only coordinated by the harder base ammonia, which leads to isolated  $\text{As}_4^{2-}$  anions, which are quite soft bases, in compound **1**. As a result, direct coordination of lithium cations to poly-anions in ammoniates is rare, one example is  $[\text{Li}(\text{NH}_3)_4]_3[\text{Li}_2(\text{NH}_3)_2\text{Sb}_5] \cdot 2\text{NH}_3$  with an ion-paired  $[\text{Li}_2(\text{NH}_3)_2\text{Sb}_5]^{3-}$  complex built around *cyclo*- $\text{Sb}_5^{5-}$  [23]. In compound **2**, sodiumpentaammine complexes take the role of the lithiumtetra-



**Fig. 4.** Detail of the structure of  $[\text{Na}(\text{NH}_3)_5]_2\text{As}_4 \cdot 3\text{NH}_3$ ; ellipsoids are drawn with a probability factor of 70%; hydrogen atoms are only shown when they are part of hydrogen bonds; distances (in Å) and angles (in  $^\circ$ ): As(1)–As(2) 2.3439(8), As(2)–As(3) 2.3453(8), Na(1)–N(2) 2.443(4), Na(1)–N(5) 2.459(4), Na(1)–N(3) 2.490(5), Na(1)–N(4) 2.496(4), Na(1)–N(1) 2.592(4), N(7)–N(7)#2 0.87(2); As(2)–As(1)–As(2)#1 90.47(4), As(1)–As(2)–As(3) 89.57(2), As(2)–As(3)–As(2)#1 90.40(4), N(2)–Na(1)–N(5) 129.60(2), N(2)–Na(1)–N(3) 111.5(2), N(5)–Na(1)–N(3) 118.4(2), N(2)–Na(1)–N(4) 89.7(1), N(5)–Na(1)–N(4) 91.7(1), N(3)–Na(1)–N(4) 95.9(2), N(2)–Na(1)–N(1) 89.3(1), N(5)–Na(1)–N(1) 90.3(1), N(3)–Na(1)–N(1) 82.8(2), N(4)–Na(1)–N(1) 177.9(2); hydrogen bonds: N(1)··N(7)#3 3.22(1), N(1)··N(7)#4 3.34(1), N(3)··N(7)#5 3.376(9), N(4)··N(7)#5 3.38(1), N(5)··N(7)#4 3.383(9), N(6)··N(7) 3.07(1), N(6)··N(7)#2 3.37(1); H(1C)··N(7)#3 2.47, H(1C)··N(7)#4 2.63, H(3A)··N(7)#5 2.49, H(4B)··N(7)#5 2.49, H(5A)··N(7)#4 2.66, H(6C)··N(7) 2.03(4), H(6C)··N(7)#2 2.38(4); N(1)–H(1C)··N(7)#3 140.7, N(1)–H(1C)··N(7)#4 135.2, N(3)–H(3A)··N(7)#5 165.3, N(4)–H(4B)··N(7)#5 165.0, N(5)–H(5A)··N(7)#4 137.1, N(6)–H(6C)··N(7) 158(5), N(6)–H(6C)··N(7)#2 151(5); symmetry operations: #1 =  $-x + 1/2, y, -z$ ; #2 =  $-x + 1/2, -y + 3/2, -z + 1/2$ ; #3 =  $x - 1/2, -y + 1, z$ ; #4 =  $-x + 0, y - 1/2, -z + 1/2$ ; #5  $x, y - 1, z$

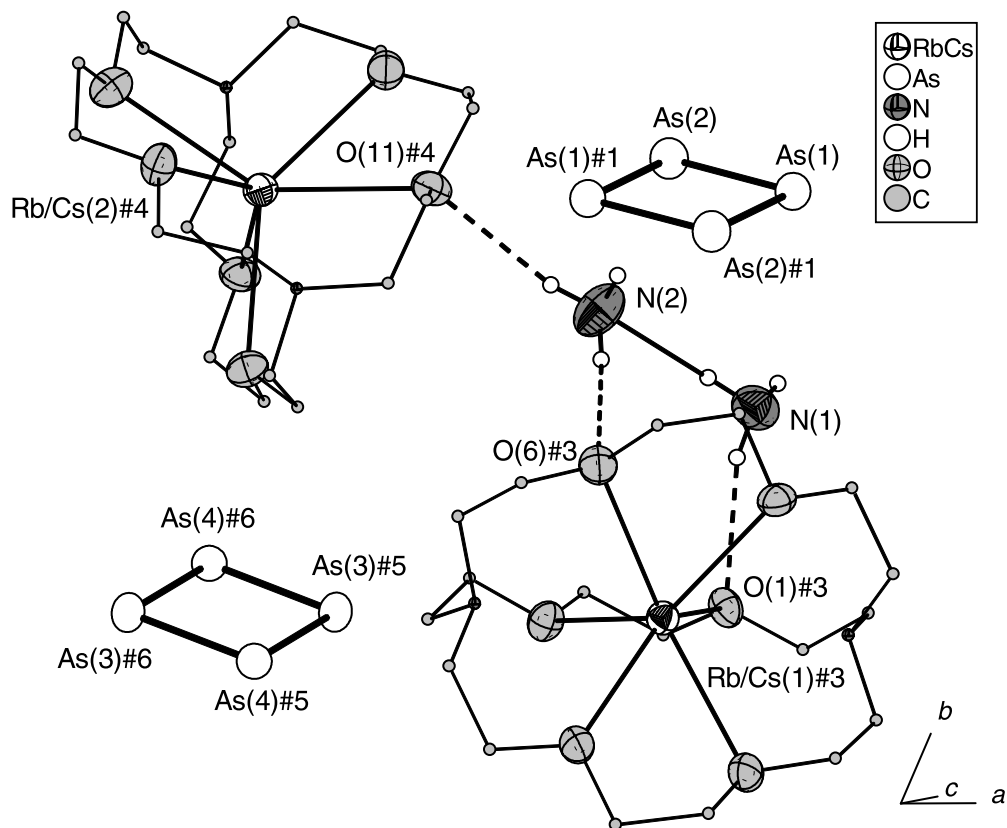
ammine complexes in **1**. Sodium cations form less stable ammine complexes but however, have also a low tendency to coordinate to polyarsenide anions. Rubidium and cesium cations are softer acids – in comparison to lithium or sodium cations – and usually form complexes with polyarsenide or polyphosphide anions like in  $[\text{N}(\text{CH}_3)_4]_2\text{RbAs}_7 \cdot \text{NH}_3$  [24] or in  $\text{Cs}_3\text{P}_7 \cdot 3\text{NH}_3$  [25]. But the stronger tendency of polycyclic chelating polyether ligands like *2,2,2-crypt* to form alkali metal



**Fig. 5.** Projection of the unit cell contents of  $[\text{Rb}_{0.65}\text{Cs}_{0.35}(2,2,2\text{-crypt})]_2\text{As}_4 \cdot 2\text{NH}_3$  on the  $bc$ -plane showing the  $[\text{Cs}_{0.35}\text{Rb}_{0.65}(2,2,2\text{-crypt})]^+$  complexes in polyhedral design; hydrogen atoms are omitted for clarity

cation complexes can prevent direct contacts between cations and anions, which can be seen in **3**. In fact, corresponding monocyclic ligands like *18C6* (1,4,7,10,13,16-Hexaoxacyclooctadecan) do not prevent direct anion-cation contacts but lead to ion-paired neutral molecules like in  $[\text{Rb}(18\text{C}6)]_3\text{As}_7 \cdot 8\text{NH}_3$  [18] or  $[\text{Cs}(18\text{C}6)]_2\text{Bi}_2 \cdot 7\text{NH}_3$  [26].

The *cyclo*-tetraarsendiide anions in compounds **1–3** are planar and of almost square geometry, although the required crystallographic point group symmetry of the  $\text{As}_4^{2-}$  anion is only  $C_i$  (**1**, **3**) and  $C_2$  (**2**). All dihedral angles are  $0^\circ$  by symmetry and both the As–As distances and the As–As–As angles vary only marginally. The mean As–As distance of 2.366 Å in the  $\text{As}_4^{2-}$  anions is distinctly shorter than the As–As distance in the skutterudite-type structure of  $\text{CoAs}_3$  formally containing  $\text{As}_4^{4-}$  anions (mean distance of 2.463 Å) [14], but very similar to those in  $\text{As}_6^{4-}$  (2.380 Å) [15]. The  $\text{As}_4^{2-}$  anion is one of the few examples of homoatomic group 15 polyanions with a formal bond order higher than one (1.5 as from a *Frost-Musulin* diagram) and adds to a series of analogous  $E_4^{2-}$  anions [27, 28]  $\text{P}_4^{2-}$  in  $\text{Cs}_2\text{P}_4 \cdot 2\text{NH}_3$  [27],  $\text{Sb}_4^{2-}$  in  $[\text{K}(2,2,2\text{-crypt})]_2\text{Sb}_4$  [29], and  $\text{Bi}_4^{2-}$  in  $[\text{A}(2,2,2\text{-crypt})]_2\text{Bi}_4$  ( $A = \text{K}, \text{Rb}$ ) [30, 31].



**Fig. 6.** Detail of the structure of  $[\text{Cs}_{0.35}\text{Rb}_{0.65}(2,2,2\text{-crypt})]_2\text{As}_4 \cdot 2\text{NH}_3$ ; ellipsoids are drawn with a probability factor of 70%; distances (in Å) and angles (in °): As(1)–As(2)#1 2.3812(8), As(1)–As(2) 2.3852(8), As(3)#6–As(4)#5 2.3797(8), As(3)#6–As(4)#6 2.3857(8); As(2)#1–As(1)–As(2) 89.88(3), As(1)#1–As(2)–As(1) 90.12(3), As(4)#5–As(3)#6–As(4)#6 90.31(3), As(3)#5–As(4)#6–As(3)#6 89.69(3); hydrogen bridges: N(1)··O(1)#3 3.221(7), N(1)··N(2) 3.347(8), N(2)··O(11)#4 3.354(7), N(2)··O(6)#3 3.424(7); H(1BN)··O(1)#3 2.38(7), H(1CN)··N(2) 2.49(7), H(2BN)··O(11)#4 2.56(8), H(2CN)··O(6)#3 2.57(8); N(1)–H(1BN)··O(1)#3 163(8), N(1)–H(1CN)··N(2) 158(8), N(2)–H(2BN)··O(11)#4 143(8), N(2)–H(2CN)··O(6)#3 159(10); symmetry operations: #1 =  $-x, -y + 1, -z + 1$ ; #2 =  $-x + 2, -y + 2, -z$ ; #3 =  $x, y - 1, z$ ; #4 =  $x - 1, y, z$ ; #5 =  $-x + 1, -y + 1, -z$ ; #6 =  $-x + 1, -y + 1, -z$

## Experimental

All manipulations were performed under dry argon or vacuum using standard *Schlenk* techniques. Single crystals were isolated directly from the ammonia solution and measured on an Image Plate Diffraction System (IPDS STOE & Cie, graphite monochromatized  $\text{MoK}_\alpha$ -radiation) at 123 K. More information on the structure solution and the refinement can be found in Table 1. Hydrogen atoms of free ammonia molecules were found by difference *Fourier* analysis, if possible, and refined isotropically with a N–H distance restraint. Hydrogen atoms in lithiumtetraamine and sodiumpentaamine complexes were found by local ring *Fourier* synthesis and refined isotropically using a riding model. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe (FIZ), D-76344 Eggenstein-Leopoldshafen, or from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ (UK), on quoting the deposition numbers CSD-415257 (1), CCDC-174984 (2), and CCDC-267197 (3).



**Table 1.** Crystal data and structure refinement data for [Li(NH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>As<sub>4</sub> (**1**), [Na(NH<sub>3</sub>)<sub>5</sub>]<sub>2</sub>As<sub>4</sub> · 3NH<sub>3</sub> (**2**), and [Cs<sub>0.35</sub>Rb<sub>0.65</sub>(2,2,2-*crypt*)]<sub>2</sub>As<sub>4</sub> · 2NH<sub>3</sub> (**3**)

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	H <sub>24</sub> As <sub>4</sub> Li <sub>2</sub> N <sub>8</sub>	H <sub>39</sub> As <sub>4</sub> N <sub>13</sub> Na <sub>2</sub>	C <sub>36</sub> H <sub>78</sub> As <sub>4</sub> Cs <sub>0.7</sub> N <sub>6</sub> O <sub>12</sub> Rb <sub>1.30</sub>
Formula weight/g mol <sup>-1</sup>	449.83	567.08	1289.97
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>I</i> 2/ <i>a</i> (No. 15)	<i>P</i> $\bar{1}$ (No. 2)
Cell parameters	<i>a</i> = 11.851(1) Å <i>b</i> = 10.410(1) Å <i>c</i> = 13.721(1) Å  <i>β</i> = 92.75(1)°  <i>V</i> = 1690.8(2) Å <sup>3</sup>	<i>a</i> = 12.042(1) Å <i>b</i> = 12.287(1) Å <i>c</i> = 16.122(1) Å  <i>β</i> = 98.53(1)°  <i>V</i> = 2359.0(3) Å <sup>3</sup>	<i>a</i> = 11.358(1) Å <i>b</i> = 13.782(2) Å <i>c</i> = 19.573(3) Å <i>α</i> = 79.71(1)° <i>β</i> = 73.149(9)° <i>γ</i> = 66.88(1)° <i>V</i> = 2689.5(6) Å <sup>3</sup>
Formula units per unit cell	4	4	2
Calculated density/Mg m <sup>-3</sup>	1.767	1.588	1.593
Absorption coefficient/mm <sup>-1</sup>	7.820	5.662	4.152
Absorption correction	Empirical, DELREFABS [32]		
<i>F</i> (000)/ <i>e</i>	872	1124	1300
<i>θ</i> -range/°	2.46–25.98	2.09–25.89	2.18–28.01
Total number of reflections	9501	16220	47412
Independent reflections	1898	2211	11998
<i>R</i> <sub>int</sub>	0.0728	0.0677	0.0704
Structure solution	Direct methods, SHELXS-97 [33]		
Structure refinement	Least square refinement ( <i>F</i> <sup>2</sup> ), SHELXL-97 [34]		
Parameters	135	106	605
Goodness-of-fit ( <i>F</i> <sup>2</sup> )	1.018	0.857	0.978
<i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0489	0.0332	0.0393
<i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.1326	0.0666	0.0981
<i>R</i> <sub>1</sub> (all reflections)	0.0677	0.0746	0.0673
<i>wR</i> <sub>2</sub> (all reflections)	0.1421	0.0751	0.1038
Largest difference peaks/ <i>e</i> Å <sup>-3</sup>	0.653 / -0.651	0.586 / -0.324	1.214 / -0.727

*[Li(NH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>As<sub>4</sub>*

In a Schlenk tube, 1.78 g (23.8 mmol) grey metallic arsenic and 0.15 g (21.6 mmol) metallic lithium were placed together with 1.21 g (30.2 mmol) elemental calcium and 0.06 g (2.2 mmol) aluminum powder. About 25 ml dry ammonia were condensed on the educts. After several weeks of storage at 233 K, deeply red block-shaped crystals had formed. Unfortunately the crystal used in measurement turned out to be non-merohedrally twinned. Thus, only reflections of the main component were used in the structure solution and refinement.

*[Na(NH<sub>3</sub>)<sub>5</sub>]<sub>2</sub>As<sub>4</sub> · 3NH<sub>3</sub>*

Yellow crystals of **2** were obtained from ammonia solutions (25 ml) of 1.12 g (15.0 mmol) arsenic and 0.17 g (7.5 mmol) sodium stored at 233 K for several days. Because N(7) is less than 0.45 Å away from an inversion centre, it was refined with an occupancy factor of 0.5.

*[Cs<sub>0.35</sub>Rb<sub>0.65</sub>(2,2,2-*crypt*)]<sub>2</sub>As<sub>4</sub> · 2NH<sub>3</sub>*

Rb<sub>4</sub>As<sub>6</sub> was prepared in evacuated glass ampoules according to the procedure given in Ref. [15]. CsPH<sub>2</sub> was prepared by passing PH<sub>3</sub> through a solution of cesium in liquid ammonia until decolour-

isation was complete, and subsequent evaporation of ammonia. 0.100 g (0.126 mmol)  $\text{Rb}_4\text{As}_6$  and 0.042 g (0.253 mmol)  $\text{CsPH}_2$  were dissolved in 20 ml liquid ammonia together with 0.200 g (0.531 mmol) 2,2,2-*crypt*. Compound **3** crystallised as orange plate-like crystals after storing the reaction vessel at 233 K for several days. Both cationic sites were refined independently to occupation factors of 0.627(6)/0.373(5) and 0.68(2)/0.32(1) for Rb/Cs at site 1 and site 2, respectively.

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