Syntheses and Crystal Structures of Four New Ammoniates with Heptaarsenide (As_7^{3-}) Anions

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The syntheses and X-ray single-crystal low-temperature structures of the four new ammoniates $[Li(NH_3)_4]_3As_7 \cdot NH_3$ (**1**), $[Rb(18\text{-crown-}6)]_3As_7 \cdot 8\,NH_3$ (**2**), $Cs_3As_7 \cdot 6\,NH_3$ (**3**), and $(Ph_4P)_2CsAs_7 \cdot 5\,NH_3$ (**4**) are reported. The compounds were obtained by either direct reduction of As with Li/Cs in liquid NH_3, solvation of Cs_4As_6/Rb_4As_6 in liquid NH_3, or by extraction of solid Cs_3As_7. While compound **1** contains isolated As_7^{3-} polyanions, As–M contacts (M = Na – Cs) lead to neutral $[Rb(18\text{-crown-}6)]_3As_7$ units in **2**, a three-dimensional, extended network in **3**, and one-dimensional, infinite $^1_\infty[CsAs_7]^{2-}$ chains in **4**, respectively.

Introduction. – Binary compounds between arsenic and alkali or alkaline earth metals containing polyarsenide anions have been less intensively investigated than the corresponding polyphosphide compounds. Nevertheless, a number of different molecular anions have been reported so far. In the 1930s, *Zintl* and co-workers published electrochemical studies of Na/As alloys, where the compound Na_3As_7 was mentioned [1]. Ba_3As_{14} was the first compound containing a heptaarsenide (As_7^{3-}) anion investigated by single-crystal X-ray crystallography [2]. Since then, related compounds of the type $M^I_3As_7$ (M = Li – Cs) have been synthesized by high-temperature reactions from the elements for all alkali metals [3–6]. Alternatively, reactions in organic solvents with precursors such as lithium-tetrakis(silylarsanyl)alanate or lithium-bis(trimethylsilyl)arsanide-tetrahydrofuran yielded the same nortricyclane analogous anion (see *Fig. 1* below) in $[Li(TMEDA)]_3As_7 \cdot OEt_2$ or $[Li(DME)]_3As_7 \cdot OEt_2$ [7][8]. The As_7^{3-} anion can be converted into neutral As_7R_3 (R = Me_3Si, Me_3Ge, Me_3Sn) molecules by introducing R *via* the corresponding chlorides (R–Cl) [9]. The second well-known cage-like polyarsenide anion is As_{11}^{3-}, which was first found in $[K(2,2,2\text{-crypt})]_3As_{11}$ [10], synthesized by the extraction of a solid with nominal composition KAs_2 with ethylenediamine. Later, As_{11}^{3-} was also found in the binary compounds $M^I_3As_{11}$ (M = Na – Cs) [11][12], which were synthesized by high-temperature reactions from the elements or from $M^I_3As_7$ and additional As. In the compound $[Rb(2,2,2\text{-crypt})]_4As_{22} \cdot 4$ DMF [13], two As_{11}^{3-} cages are connected by oxidative coupling between two of the formerly divalent As-atoms, yielding the anion As_{22}^{4-}. Similarly, in $[K(2,2,2\text{-crypt})]_4SnAs_{14}$, two As_7^{3-} anions are connected by a Sn-atom, forming a $SnAs_{14}^{4-}$ anion [13]. Planar cyclic polyarsenide anions are As_4^{4-}, As_6^{4-}, and As_4^{2-}. The first can be found in the skutterudite structure of $CoAs_3$. As_6^{4-} occurs in Rb_4As_6 and Cs_4As_6 , which were obtained by classical high-temperature reactions from the elements [14]. $[Na(NH_3)_5]_2As_4 \cdot 3\,NH_3$, containing the As_4^{2-} anion, was synthesized in our group by direct reduction of As with Na in liquid NH_3 [15]. $Na_4Ba_3As_6$ [16] and

K_5As_4 [17] are examples for compounds with finite-chain polyarsenide anions. While $Na_4Ba_3As_6$ contains the 'normal' As_3^{5-} anion, the situation in K_5As_4 is more complicated, as the anionic part of the structure can be best described as an As_4^{4-} anion plus an extra delocalized electron.

Liquid NH_3 is a good solvent for alkali metal heptaarsenides. However, NH_3 is often incorporated into the compounds crystallizing from these solutions, resulting in ammoniates like $Cs_3As_7 \cdot NH_3$ [18] and $(Me_4N)_2RbAs_7 \cdot NH_3$ [19]. Thereby, the former was obtained from an NH_3 solution of Cs_3As_7, while the latter was prepared by partial ion exchange of Rb_3As_7 with $Me_4N^+I^-$ in liquid NH_3. These two compounds are rare examples of room-temperature-stable ammoniates, the majority of ammonia 'solvated' crystals being thermally unstable above *ca.* $-10°$. By means of low-temperature crystallographic techniques, the structural characterization of such unstable ammoniates is possible nowadays.

In this contribution, four new ammoniate compounds containing As_7^{3-} anions were synthesized from elemental As and alkali metal arsenides in liquid NH_3, and their structures were elucidated by means of single-crystal X-ray analysis.

Results. – The four new compounds $[Li(NH_3)_4]_3As_7 \cdot NH_3$ (**1**), [Rb(18-crown-6)]$_3$As$_7 \cdot 8\,NH_3$ (**2**), $Cs_3As_7 \cdot 6\,NH_3$ (**3**), and $(Ph_4P)_2CsAs_7 \cdot 5\,NH_3$ (**4**) were prepared *via* different routes¹). Direct reduction of the grey elemental modification of As in liquid NH_3 by either Li or Cs resulted in the formation of **1** and **3**, respectively. Extraction of solid Cs_3As_7/Cs_3As_{11} also results in **3**, as well as solvation of solid Cs_4As_6 in liquid NH_3 in the presence or absence of 18-crown-6. Compounds **2** and **4** were obtained from NH_3 solutions of the corresponding heptaarsenides in the presence of either 18-crown-6 or $Ph_4P^+I^-$.

Compounds **1**–**4** all contain the known As_7^{3-} anion, which has a structure analogous to nortricyclane (see below) [20]. However, the new compounds were found to differ significantly with respect to the chemical environment of the heptaarsenide anion in the respective crystals. In **1**, the As_7^{3-} anions were not in direct contact with the Li^+ cations. In contrast, coordination of the As_7^{3-} cage by Cs^+ resulted in a framework structure for **3**. A similar coordination between Cs^+ and As_7^{3-} anions was found in the crystal structure of **4**. However, due to the presence of the large, non-coordinating tetraphenylphosphonium (Ph_4P^+) cations, giving rise to a reduction of the Cs–As contacts, one-dimensionally extended $^1_\infty[CsAs_7]^{2-}$ chains were observed. Finally, in the case of **2**, the addition of better alkali metal ligands than NH_3 led to neutral, molecular complexes of As_7^{3-} with Rb^+ and crown ether molecules.

In an ideal case, the As_7^{3-} structure is C_{3v}-symmetric and can be described as As_4 tetrahedrons with three bridged edges (*Fig. 1*). The bonding distances in all ionic nortricyclanes show a characteristic distribution of three types of bonds, with $A > C > B$. The distances A are defined by the three atoms of the triangular base, distances B are those between the base atoms and the bridging atoms, and C refers to the distances between the bridging atoms and the apical atom. The ratio $Q = H/A_m$ [21], where H is the height of the anion (from the base to the apical atom) and A_m is mean value of

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¹) 18-Crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane.

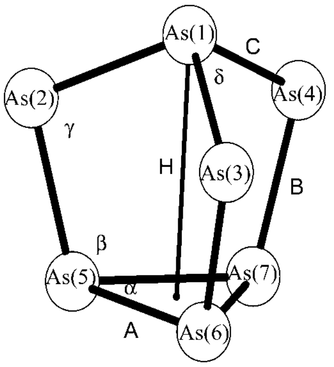

Fig. 1. *Structure of an 'ideal' As_7^{3-} cage anion*. Three distances *A* – *C* and the height *H* of the cage are indicated.

distances *A*, typically lies between 1.31 and 1.35 for ionic nortricyclane systems, in contrast to 1.42 for neutral, covalently substituted cages [18].

Crystal Structure of $[Li(NH_3)_4]_3As_7 \cdot NH_3$ (**1**). In *Fig. 2*, a projection of the unit cell of **1** is shown. The compound contains discrete As_7^{3-} cages, $[Li(NH_3)_4]^+$ cations, and NH_3 'solvation' molecules. The characteristic structural features of the As_7^{3-} cages are listed in *Table 1*. The $[Li(NH_3)_4]^+$ units are of approximately tetrahedral shape, with Li–N distances of 2.03(3) – 2.12(3) Å, and N–Li–N angles of 103(1) – 125(1)°. Such homoleptic $[Li(NH_3)_4]^+$ complexes are the dominating cations in lithium ammoniates [22 – 24], whereas direct coordination of Li^+ to polyanionic clusters is rare, one example being $[Li(NH_3)_4]_3[Li_2(NH_3)_2Sb_5] \cdot 2\ NH_3$, with an ion-paired $[Li_2(NH_3)_2Sb_5]^{3-}$ complex built around cyclo-Sb_5^{5-} [25]. The single NH_3 molecule per asymmetric unit (N(13)) connects two $[Li(NH_3)_4]$ units *via* H-bonds, N(13) being the acceptor of a forked N–H ··· N H-bond, and the relevant H-atoms are attached to N(11) and N(1)#1 (see *Fig. 2*). The N ··· H distances (2.56 and 2.39 Å) agree well with previous results for other solid ammoniates [26] [27].

Table 1. *Average Distances and Angles in the As_7^{3-} Units of Compounds* **1** – **4**. For abbreviations, see *Fig. 1.* Compounds: $[Li(NH_3)_4]_3As_7 \cdot NH_3$ (**1**), $[Rb(18\text{-crown-}6)]_3As_7 \cdot 8\ NH_3$ (**2**), $Cs_3As_7 \cdot 6\ NH_3$ (**3**), and $(Ph_4P)CsAs_7 \cdot 5\ NH_3$ (**4**).

	1	**2**	**3**	**4**
A_m [Å]	2.50	2.524	2.515	2.522
B_m [Å]	2.34	2.361	2.343	2.351
C_m [Å]	2.40	2.421	2.404	2.424
δ_m [°]	101.1	101.6	101.3	101.1
γ_m [°]	99.5	99.0	99.5	99.4
β_m [°]	105.0	105.2	104.9	105.1
H [Å]	3.318(3)	3.3329(7)	3.320(1)	3.3395(5)
$Q = H/A_m$	1.33	1.32	1.32	1.31

Crystal Strucutre of $[Rb(18\text{-crown-}6)]_3As_7 \cdot 8\ NH_3$ (**2**). In compound **2**, the As_7^{3-} anion is surrounded by three Rb^+ cations, which, in turn, are coordinated by one crown ether molecule each; this results in a neutral $[Rb(18\text{-crown-}6)]_3As_7$ complex (*Fig. 3*).

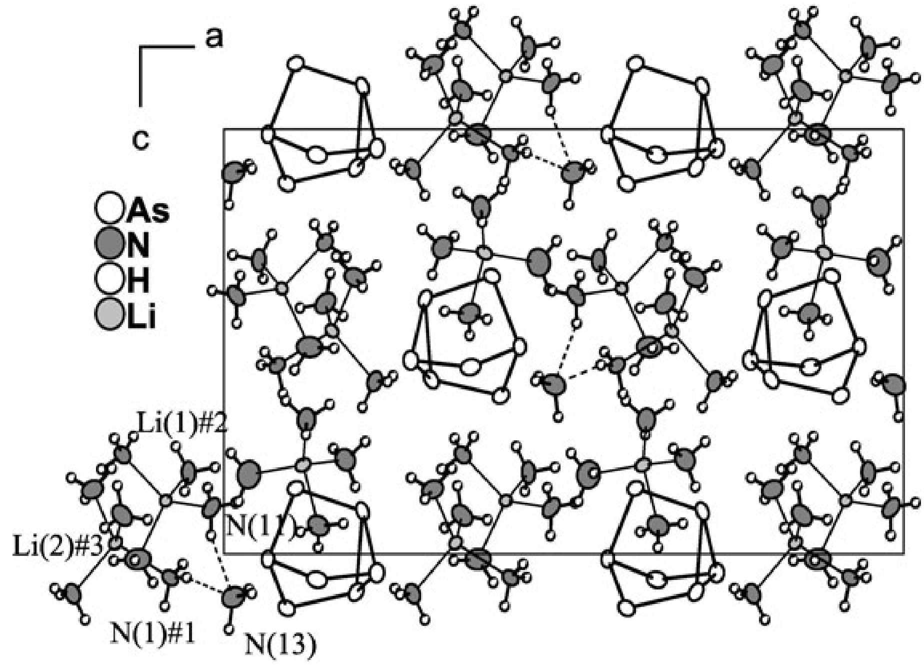

Fig. 2. *Projection of the X-ray structure of* $[Li(NH_3)_4]_3As_7 \cdot NH_3$ (**1**) *on the* ac*-plane.* H-bonds (N–H···H) are indicated. Ellipsoids were drawn at the 70% probability level. Selected distances (in Å): N(13)–H(11c), 2.56; N(13)–H(1a)#1, 2.39; N(13)–N(11), 3.38(2); N(13)–N(1)#1, 3.25(1). Selected angles (in °): N(1)#1–H(1a)#1–N(13), 164.3; N(11)–H(11c)–N(13), 153.4. Symmetry operations: #1 = $(x, -1+y, z)$; #2 = $(-0.5+x, 0.5-y, z)$; #3 = $(-x, -y, 0.5+z)$.

The Rb^+ cations are mainly attached to the two-bonded As-atoms of the cage, where the negative charges are formally located. The corresponding Rb–As distances range from 3.5084(6) to 3.6278(6) Å; the contacts to As(7) and As(6) at the triangular base of the anion, with 3.7088(7) and 3.7175(6) Å, respectively, are additionally included into the coordination sphere of Rb(1). All the other Rb–As distances are significantly larger (the next distance, Rb(3)–As(5), amounts to 3.9349(7) Å). The coordination of the cations by the crown ether ligands displays the usual eccentricity, the distances between the planes defined by the six O-atoms of each crown ether molecule and the corresponding Rb^+ ions being 1.290(1), 1.201(1), and 1.212(1) Å for Rb(1), Rb(2), and Rb(3), respectively.

All NH_3 molecules in **2** are involved in either N–H···N or N–H···O H-bonds, which connect atoms both within the $[Rb(18\text{-crown-}6)]_3As_7$ subunit as well as between them. Unfortunately, the NH_3 H-atoms could not be located for N(2) and N(6). However, due to the short distances to either O(6) (3.260(7)) and O(18) (3.375(7) Å), or N(4)#2 (3.30(1)) and N(7) (3.37(1) Å), H-bonding between these atoms is very probable, since these distances agree well with those found for the other six NH_3 molecules (average N···O and N···N distances of 3.35 and 3.41 Å, resp.; see *Fig. 3*). These H-bonds lead to the formation of ${}^2_\infty[(Rb(18\text{-crown-}6))_3(As_7)(NH_3)_8]$ layers that lie parallel to the *bc*-plane (*Fig. 4*).

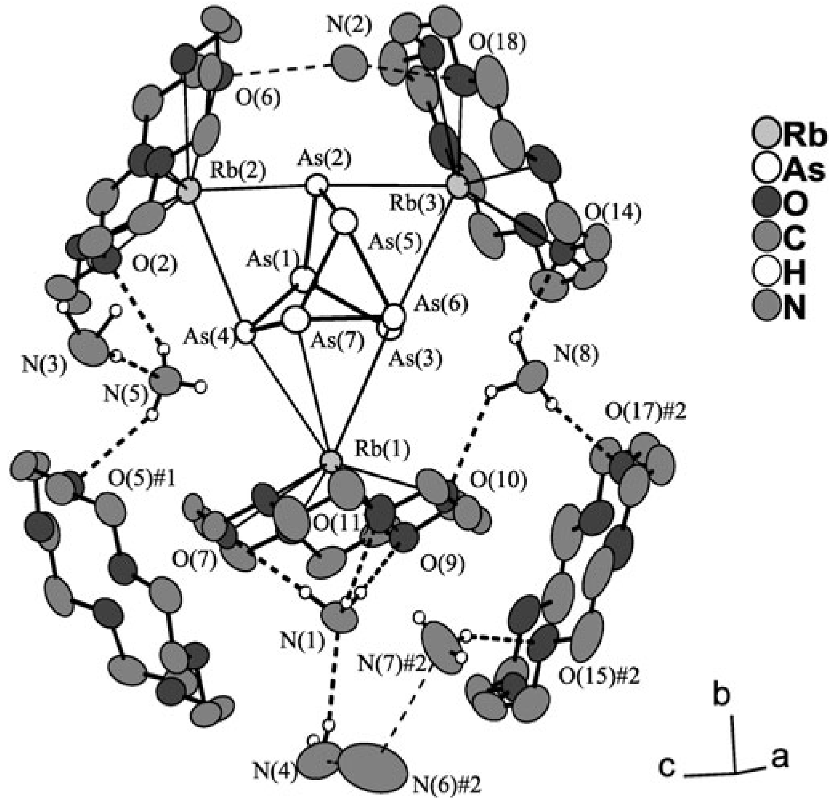

Fig. 3. *Detail of the structure of [Rb(18-crown-6)]$_3$As$_7$·8 NH$_3$* (**2**) *showing the central molecular complex and the H-bonds.* The crown ether H-atoms were omitted for clarity. Ellipsoids were drawn at the 70% probability level. Selected distances (in Å): As(1)–As(2), 2.4186; As(1)–As(3), 2.4200(7); As(1)–As(4), 2.4251(6); As(2)–As(5), 2.3566(8); As(3)–As(6), 2.3707(8); As(4)–As(7), 2.3567(7); As(5)–As(7), 2.5117(7); As(5)–As(6), 2.5199(7); As(6)–As(7), 2.5417(7); Rb(1)–As(4), 3.6076(6); Rb(1)–As(3), 3.6080(6); Rb(1)–As(6), 3.7088(7); Rb(2)–As(2), 3.5084(6); Rb(2)–As(4), 3.6278(6); Rb(3)–As(2), 3.5270(7); Rb(3)–As(3), 3.6112(6); O(7)–H(1bN), 2.37(7); O(7)–N(1), 3.390(7); O(11)–H(1cN), 2.63(7); O(11)–N(1), 3.534(7); O(9)–H(1aN), 2.38(7); O(9)–N(1), 3.311(6); N(1)–H(4bN), 2.50(6); N(1)–N(4), 3.297(9); N(4)–N(6)#2, 3.30(1); N(6)#2–N(7)#2, 3.366(9); O(15)#2–H(7aN)#2, 2.50; O(15)#2–N(7)#2, 3.357(7); O(10)–H(8aN), 2.59(7); O(10)–N(8), 3.420(7); O(17)#2–H(8bN), 2.35(6); O(17)#2–N(8), 3.272(6); O(14)–H(8cN), 2.4(1); O(14)–N(8), 3.272(6); O(18)–N(2), 3.376(6); O(6)–N(2), 3.260(7); O(2)–H(5aN), 2.50; O(2)–N(5), 3.258(6); O(5)#1–H(5bN), 2.60; O(5)#1–N(5), 3.316(6); N(5)–H(3aN), 2.32(5); N(5)–N(3), 3.524(7). Selected angles (in °): O(7)–H(1bN)–N(1), 177(8); O(11)–H(1cN)–N(1), 147(6); O(9)–H(1aN)–N(1), 171(8); N(1)–H(4bN)–N(4), 164(8); O(15)#2–H(7aN)#2–N(7)#2, 158.1; O(10)–H(8aN)–N(8), 133(5); O(17)#2–H(8bN)–N(8), 155(6); O(14)–H(8cN)–N(8), 129(8); O(2)–H(5aN)–N(5), 140.7; O(5)#1–H(5bN)–N(5), 135.7; N(5)–H(3aN)–N(3), 175(6). Symmetry operations: #1 = $(0.5 - x, -0.5 - y, 2.5 - z)$; #2 = $(0.5 - x, -0.5 + y, 1.5 - z)$.

Crystal Strucutre of Cs$_3$As$_7$·6 NH$_3$ (**3**). In compound **3**, the As_7^{3-} anions are situated on a threefold crystallographic axis of the trigonal space group *R*3*c*, As(1) being on the special position *6a*, and As(2) and As(3) on general position *18b*, thus generating the seven-atom cage by site symmetry (*Fig. 5*). One Cs$^+$ and two NH$_3$ on general positions complete the asymmetric unit of **3**.

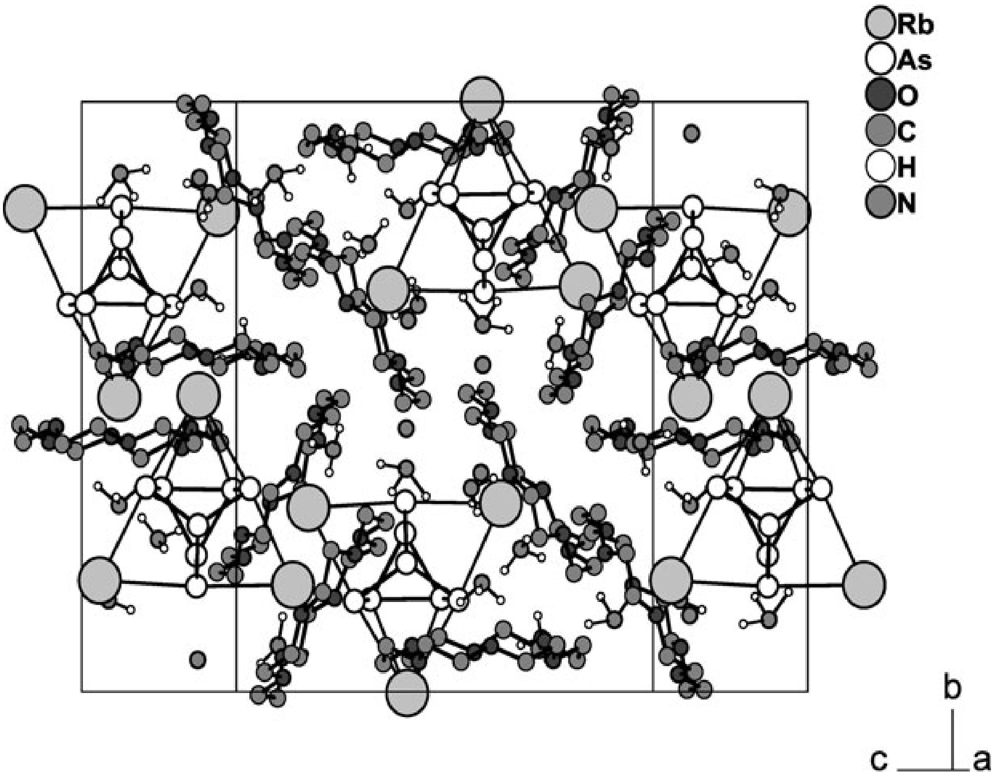

Fig. 4. *Projection of the X-ray structure of [Rb(18-crown-6)]$_3$As$_7$ · 8 NH$_3$* (**2**) *on the* cb-*plane*

Each As_7^{3-} is surrounded by nine Cs^+, with distances between 3.7171(6) and 4.0082(7) Å. Each trapezoid side of the As_7^{3-} (built of the two-bonded As-atoms and those of the triangular base) is coordinated η^4-like by one Cs^+. One additional Cs^+ coordinates η^1-like to each of these six As-atoms with a similar distance (see *Fig. 5*). The mean Cs–As distance is *ca.* 5% shorter for the coordination at the two-bonded As-atoms (3.7672 Å) than for the three-bonded arsenic atoms (3.9464 Å), which could indicate stronger interactions of Cs^+ with the formally negatively charged As-atoms. The corresponding coordination sphere of Cs^+ in **3** is shown in *Fig. 6*. In addition to the six As-atoms of three cages, Cs(1) is coordinated by two NH_3, with distances of 3.322(6) Å and 3.304(5) Å. The multiple coordinative interactions between Cs^+ and the cage anions lead to a dense three-dimensional (3D) $^3_\infty[Cs_3As_7]$ network, with NH_3 molecules in small interstices – a situation very similar to that in $Cs_3As_7 \cdot NH_3$ [18].

Crystal Structure of [Ph$_4$P]$_2$CsAs$_7$ · 5 NH$_3$ (**4**). In compound **4**, the single Cs^+ cation in the asymmetric unit is coordinated by two adjacent As_7^{3-} cages in a fashion such that $^1_\infty[CsAs_7]^{2-}$ zigzag chains are formed (*Fig. 7*). These chains are separated by the large, non-coordinating Ph_4P^+ cations. Cs(1) is coordinated by totally eight As-atoms of the heptaarsenide anions, two of the three trapezoid sides of each As_7^{3-} cage being capped η^4-like by one Cs^+. The Cs–As distances lie in the range of 3.6336(4) to 3.9380(3) Å

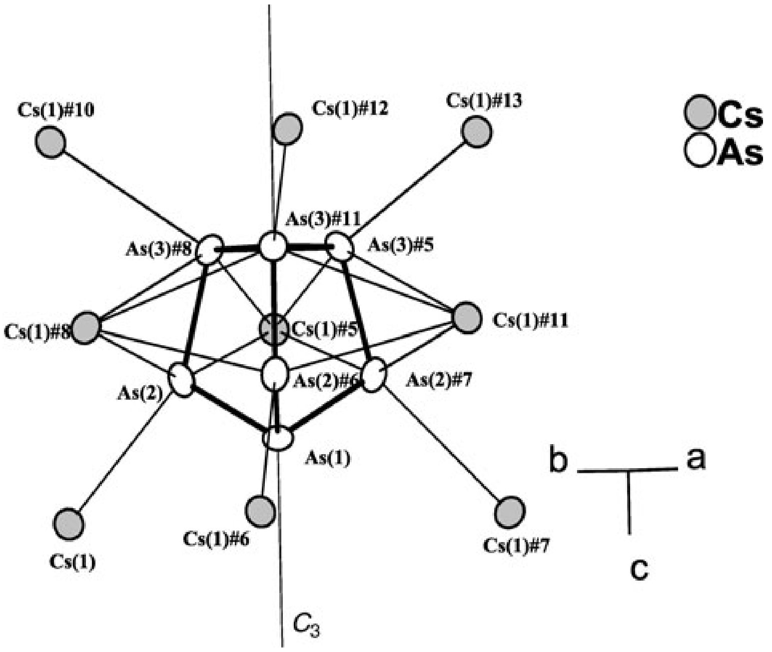

Fig. 5. *Coordination sphere of* As_7^{3-} *in* $Cs_3As_7 \cdot 6\,NH_3$ (**3**). Ellipsoids were drawn at the 70% probability level. Selected distances (in Å): As(1)–As(2), 2.4039(7); As(2)–As(3)#8, 2.3430(7); As(3)–As(3)#4, 2.5150(9). Selected angels (in °): As(2)#3–As(3)–As(3)#4, 60.0; As(2)#3–As(3)–As(3)#9, 104.76(2); As(2)#3–As(3)–As(3)#4, 104.98(2); As(1)–As(2)–As(3)#8, 99.52(3); As(2)–As(1)–As(2)#6, 101.30(3). Symmetry operations: #2 = $(-y+4/3, -x+5/3, z+1/6)$; #3 = $(-x+y+1/3, y-1/3, z+1/6)$; #4 = $(-y+1, x-y+1, z)$; #5 = $(-y+5/3, -x+4/3, z-1/6)$; #6 = $(-x+y+1, -x+2, z)$; #7 = $(-y+2, x-y+1, z)$; #8 = $(-x+y+2/3, y+1/3, z-1/6)$; #9 = $(-x+y, -x+1, z)$; #10 = $(-x+y+1/3, -x+5/3, z-1/3)$; #11 = $(x+2/3, x-y+4/3, z-1/6)$; #12 = $(-y+7/3, x-y+5/3, z-1/3)$; #13 = $(x+1/3, y-1/3, z-1/3)$.

(*Fig. 8*). The $^{1}_{\infty}[CsAs_7]^{2-}$ chains run parallel to the crystallographic *c*-axis. Four NH_3 molecules are connected *via* H-bonds and form finite four-membered chains, whereas the fifth NH_3 molecule remains isolated (N(5)–Cs(1) = 4.136(5) Å). The mean N ··· H distances between these ammonia molecules are 2.47 Å, and the mean N ··· N distances are 3.331 Å.

Discussion. – The differences in the dimensionality of the As_7^{3-} containing ammoniates reported here may be rationalized by the well-known HSAB principle [28]. The relatively hard *Lewis* acid Li^+ in **1** is coordinated only by the hard base NH_3, which leads to a non-coordinating $[Li(NH_3)_4]^+$ complex. As a result of this, the soft As_7^{3-} units remain isolated. The much softer Rb^+ cations in **2** coordinate the heptaarsenide anions, but due to the sequestering effect of the crown ether molecules, no higher-dimensional structure is formed. In **3**, the even softer Cs^+ is mainly coordinated to the soft As_7^{3-} anions, and, thus, a 3D network results. The decrease of dimensionality in **4** as compared to **3** is due to the non-coordinating Ph_4P^+. A single Cs^+ per As_7^{3-} cannot afford a 3D structure, but a $^{1}_{\infty}[CsAs_7]^{2-}$ chain. In their structural

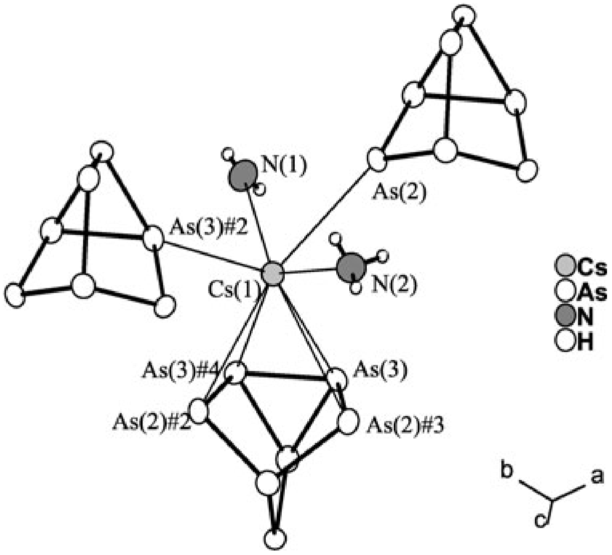

Fig. 6. *Coordination sphere of Cs^+ in $Cs_3As_7 \cdot 6\ NH_3$* (**3**). Ellipsoids were drawn at the 70% probability level. Selected distances (in Å): Cs(1)–As(2), 3.7171(6); Cs(1)–As(3), 4.0082(7); Cs(1)–As(2)#3, 3.8376(7); Cs(1)–As(2)#2, 3.7469(7); Cs(1)–As(3)#4, 3.9607(7); Cs(1)–As(3)#2, 3.8704(6); Cs(1)–N(1), 3.322(6); Cs(1)–N(2), 3.304(5). Symmetry operations: #2 = $(-y+4/3,\ -x+5/3,\ z+1/6)$; #3 = $(-x+y+1/3,\ y-1/3,\ z+1/6)$; #4 = $(-y+1,\ x-y+1,\ z)$.

effects, the Ph_4P^+ cations in **4** can be compared to the $[Li(NH_3)_4]^+$ units in **1**. Similar chains can be found in $(Me_4N)_2RbAs_7 \cdot NH_3$ [19], with ${}^1_\infty[RbAs_7]^{2-}$ chains running parallel to the crystallographic *b*-axis. Similarly varying dimensionalities of alkali metal–polypnictide substructures have already been described for the ammoniates of hepta- and undecapolyphosphides. While $Cs_3P_{11} \cdot 3\ NH_3$ [29] or $Cs_3P_7 \cdot 3\ NH_3$ [30] form 3D networks as in **3**, the dimensionality is reduced to 2D sheets ${}^2_\infty[Cs_2P_{11}]^-$ or ${}^2_\infty[Cs_2P_7]^-$ in $[Me_4N]Cs_2P_{11}$ [31] and $[EtMe_3N]Cs_2P_7 \cdot 2\ NH_3$ [32], respectively, due to the exchange of one Cs^+ ion by a quaternary ammonium ion. A further reduction of the Cs content yields ${}^1_\infty[CsP_{11}]^{2-}$ chains, which were reported for $[EtMe_3N]_2CsP_{11} \cdot 5\ NH_3$ [33]. The lack of any extended alkali metal–polypnictide substructure in **1** and **2** shows two general possibilities for the generation of such situations. One way is to use non-coordinating quaternary phosphonium/ammonium cations, or cations that preferably form non-coordinating, homoleptic complexes with NH_3, (*e.g.* Li^+). The other way is to protect coordinating cations like Rb^+ by sequestering ligands such as crown ethers. Polyphosphide representatives comparable to **1** are $[EtMe_3N]_3P_{11}$ [34] or $[Li(NH_3)_4]_3P_{11} \cdot 5\ NH_3$ [22]. Similar to the situation in **1**, in $[Li(NH_3)_4]_3P_{11} \cdot 5\ NH_3$, the $[Li(NH_3)_4]$ units are interconnected *via* H-bonds with the remaining NH_3 molecules of solvation.

The differing preparative routes used to synthesize the four presented compounds indicate that As_7^{3-} is probably the stable final product of a number of equilibria involving various polyarsenides. As both Cs_4As_6 or Rb_4As_6, which contain isometric As_6^{4-} ring anions, can be used to synthesize **2**–**4**, As_6^{4-} anions seem to be unstable in NH_3 solution.

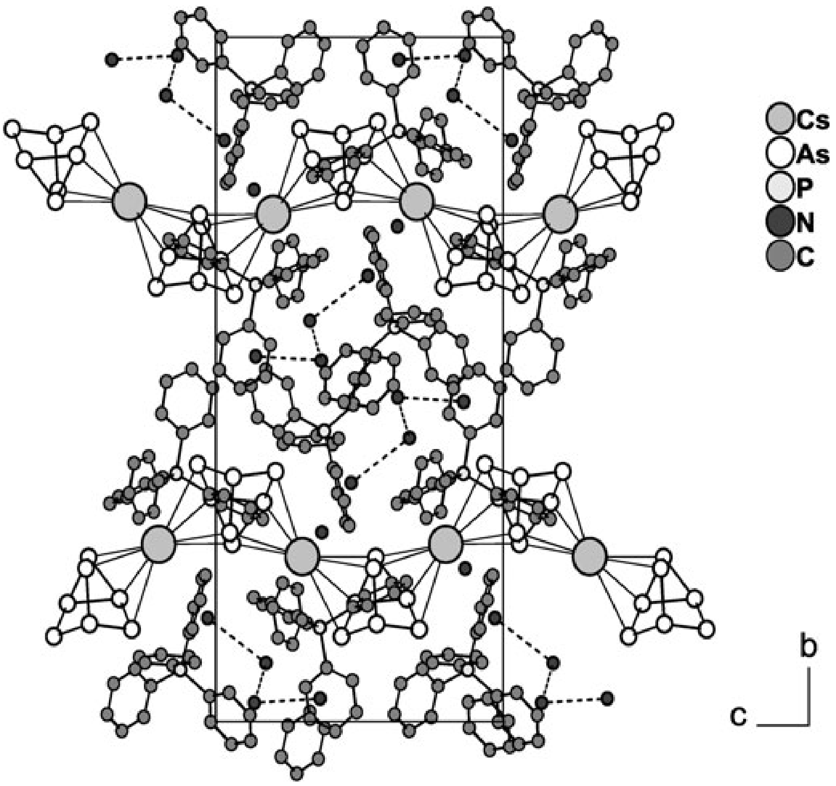

Fig. 7. *Projection of the X-ray crystal structure of* $(Ph_4P)CsAs_7 \cdot 5\,NH_3$ (**4**) *on the* cb*-plane*. The structure shows $^1_\infty[CsAs_7]^{2-}$ chains running parallel to the crystallographic *c*-axis, as well as H-bridged finite NH_3 chains. All H-atoms were omitted for clarity.

Experimental Part

General. All manipulations were performed under Ar atmosphere (O_2 and H_2O levels below 1 ppm each) or in high vacuum (*ca.* 10^{-3} mbar; oil pump) by means of standard *Schlenk* techniques. 18-crown-6 was purified by sublimation before use. Rb_4As_6 and Cs_4As_6 were prepared in an evacuated glass ampoule according to known procedures [14], as well as Cs_3As_7 and Cs_3As_{11} [11][18].

[Li(NH₃)₄]₃As₇ · NH₃ (**1**). Elemental Li (22.4 mg, 3.23 mmol) and As (1.7135 g, 22.87 mmol) were placed in a *Schlenk* tube, into which anh. liquid NH_3 (*ca.* 20 ml) was condensed at 238 K. The mixture was kept at this temp. for 5 d, which resulted in a color change from deep-blue to orange-red, accompanied by formation of red crystals of **1** with irregular shapes formed at the bottom of the vessel.

[Rb(18-crown-6)]₃As₇ · 8 NH₃ (**2**) In a *Schlenk* tube, Rb_4As_6 (78 mg, 0.099 mmol) and 18-crown-6 (0.104 g, 0.394 mmol) were placed and treated with liquid NH_3 (*ca.* 20 ml), which was condensed into the vessel at 238 K. The mixture was stored at this temp. for several days, whereupon the orange-red soln. turned green. After a few weeks, orange, octahedral crystals of **2** had grown.

Cs₃As₇ · 6 NH₃ (**3**). *Method 1.* Elemental Cs (1.8344 g, 13.8 mmol) and As (7.3625 g, 98.3 mmol) were placed in a *Schlenk* tube and treated with liquid NH_3 (*ca.* 20 ml) at 238 K. The mixture was kept at this temp. for 7 d, during which time the deep-blue soln. turned red under formation of orange-red, plate-like crystals of **3**.

Method 2. In a *Schlenk* tube, Cs_3As_{11} (0.719 g, 0.588 mmol) and Cs_3As_7 (0.543 g, 0.588 mmol) [11][18] were treated with liquid NH_3 (*ca.* 20 ml) at 238 K. The red soln. was stored at this temp. for two weeks, which resulted in the formation of cuboid, red crystals of **3**.

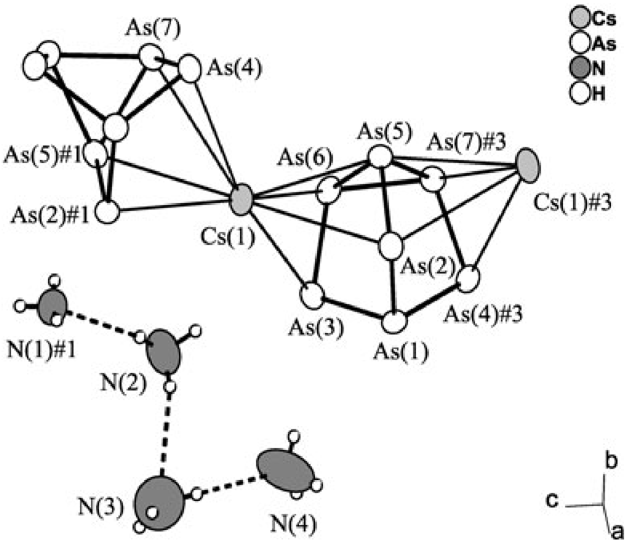

Fig. 8. *Coordination sphere of* Cs^+ *and H-bridges in* $(Ph_4P)CsAs_7 \cdot 5\,NH_3$ (**4**). Ellipsoids were drawn at the 70% probability level. Selected distances (in Å): As(1)–As(2), 2.4207(4); As(1)–As(3), 2.4244(4); As(1)–As(4)#3, 2.4278(4); As(7)#3–As(4)#3, 2.3473(4); As(6)–As(3), 2.3443(4); As(5)–As(2), 2.3611(4); As(5)–As(6), 2.5332(4); As(6)–As(7)#3, 2.5078(4); As(7)#3–As(5), 2.5250(4); Cs(1)–As(2), 3.7329(4); Cs(1)–As(2)#1, 3.7490(4); Cs(1)–As(3), 3.9362(3); Cs(1)–As(4), 3.9380(3); Cs(1)–As(5), 3.6336(4); Cs(1)–As(5)#1, 3.6531(4); Cs(1)–As(6); 3.8297(4); Cs(1)–As(7), 3.7890(4); N(1)#1–N(2), 3.407(5); N(1)#1–H(2bN), 2.57(5); N(2)–N(3), 3.410(7); N(3)–H(2cN), 2.61(4); N(3)–N(4), 3.176(9); N(4)–H(3cN), 2.23(6). Selected angles (in °): As(2)–As(1)–As(3), 101.78(1); As(3)–As(1)–As(4)#3, 101.27(4); As(4)#3–As(1)–As(2), 100.28(1); As(1)–As(2)–As(5), 99.01(1); As(1)–As(3)–As(6), 99.81(1); As(1)–As(4)#3–As(7)#3, 99.50(1); As(6)–As(5)–As(2), 105.87(1); As(7)#3–As(5)–As(2), 104.87(1); As(5)–As(6)–As(3), 104.33(1); As(7)#3–As(6)–As(3), 105.28(1); As(5)–As(7)#3–As(4)#3, 104.58(1); As(6)–As(7)#3–As(4)#3, 105.46(1); As(5)–As(6)–As(7)#3, 60.12(1); As(6)–As(7)#3–As(5), 60.44(1); As(7)#3–As(5)–As(6), 59.44(1); N(2)–H(2bN)–N(1)#1, 166(4); N(2)–H(2cN)–N(3), 160(3); N(3)–H(3cN)–N(4), 175(5). Symmetry operations: $\#1 = (x, 0.5 - y, 0.5 + z)$; $\#3 = (x, 0.5 - y, -0.5 + z)$.

Method 3. In a *Schlenk* tube, Cs_4As_6 (151 mg, 0.154 mmol) [14] and 18-crown-6 (163 mg, 0.616 mmol) were placed and reacted with liquid NH_3 (*ca.* 20 ml) at 238 K. The same reaction could also be performed without crown ether, using Cs_4As_6 (0.151 g, 0.154 mmol) and NH_3 only. Both reaction vessels were stored at 238 K for several weeks, which gave rise to orange, small, plate-like crystals of **3** in the yellow solns.

$(Ph_4P)CsAs_7 \cdot 5\ NH_3$ (**4**). In a *Schlenk* tube, Cs_4As_6 (111 mg, 0.113 mmol) [14] and $Ph_4P^+I^-$ (190 mg, 0.453 mmol) were treated with liquid NH_3 (*ca.* 20 ml) at 238 K. The yellow soln. was stored at this temp. for several weeks, which gave rise to block-shaped, black crystals of **4**.

X-Ray Crystallography. The air- and moisture-sensitive crystals of compounds **1**–**4** were taken directly from the NH_3 solns. Reflection data were measured on an *IPDS* instrument (*STOE & Cie*) with graphite-monochromated MoK_α radiation at a temperature of 123(2) K. Empirical absorption corrections were made with DELrefABS from Platon [35]. All structures were solved by direct methods with SHELXS-97 [36], and optimized by full-matrix least-squares refinement on F^2 with SHELXL-97 [37]. Details of the structure elucidations and refinements are summarized in *Table 2*. H-Atoms were located, if possible, by difference-*Fourier* analysis, and refined isotropically, or they were determined by local ring *Fourier* synthesis, and refined isotropically with a riding model. For **1**, the Li-atoms were restrained in order to approximate isotropic behavior for the corresponding U_{ij} components. The N–H distances were restrained to a standard derivation of 0.1 in **1** and **3**. Further details of the crystal-structure investigations are available on request from the *Fachinforma-*

Table 2. *Crystal Data and Structure Refinement for Compounds* **1**–**4**

	1	**2**	**3**	**4**
Structural formula	$[Li(NH_3)_4]_3As_7 \cdot NH_3$	$[Rb(18\text{-crown-}6)]_3As_7 \cdot 8\ NH_3$	$Cs_3As_7 \cdot 6\ NH_3$	$(Ph_4P)_2CsAs_7 \cdot 5\ NH_3$
Empirical formula	$H_{39}As_7Li_3N_{13}$	$C_{36}H_{96}As_7N_8O_{18}Rb_3$	$H_{18}As_7Cs_3N_6$	$C_{48}H_{55}As_7CsN_5P_2$
M_r [g/mol]	766.70	1704.01	1025.37	1421.26
Crystal size [mm]	0.1 × 0.2 × 0.2	0.1 × 0.2 × 0.2	0.3 × 0.3 × 0.3	0.5 × 0.5 × 0.3
Crystal system	orthorhombic	monoclinic	trigonal	monoclinic
Space group	$Pna2_1$ (No. 33)	$P\ 2_1/n$ (No. 14)	$R3c$ (No. 161)	$P\ 2_1/c$ (No. 14)
Cell parameters:				
a [Å]	22.326(4)	18.018(1)	13.939(1)	13.4072(7)
b [Å]	9.596(8)	19.271(1)	–	29.640(1)
c [Å]	12.628(4)	20.603(1)	20.006(1)	13.7897(7)
β [°]	–	108.149(8)	–	93.997(6)
V [Å^3]	2705(2)	6798.0(6)	3366.3(4)	5466.6(4)
Z	4	4	18	4
Density [Mg/m^3]	1.882	1.665	3.035	1.727
Abs. coeff. [mm^{-1}]	8.550	5.593	15.080	4.977
F (000)	1480	3392	2736	2776
θ [°]	1.82–23.04	2.08–25.93	2.64–25.85	2.02–25.98
Total refl.	2177	70489	4287	41922
Independent refl.	1999	13127	1430	10631
R_{int}	0.0138	0.0709	0.0313	0.0308
Completeness to θ	99.9%	98.9%	99.9%	99.2%
Parameters	232	735	73	661
Restraints	22	12	1	0
Goodness-of-fit (F^2)	1.142	0.957	0.933	1.004
R_1 ($I > 2\sigma I$)	0.0401	0.0390	0.0174	0.0236
wR_2 ($I > 2\sigma I$)	0.0880	0.0907	0.0342	0.0554
R_1 (all refl.)	0.0478	0.0593	0.0201	0.0308
wR_2 (all refl.)	0.0934	0.0961	0.0346	0.0569
Largest difference peaks [e/Å^3]	0.824, −0.760	0.808, −0.757	0.444, −0.383	0.527, −0.582

tionszentrum Karlsruhe (D-76344 Eggenstein-Leopoldshafen), on quoting the deposition numbers CSD-415189 for $[Li(NH_3)_4]_3As_7 \cdot NH_3$ (**1**) and CSD-415188 for $Cs_3As_7 \cdot 6\,NH_3$ (**3**).

The crystallographic data for the *carbon*-containing structures **2** and **4** have been deposited with the *Cambridge Crystallographic Data Centre* (*CCDC*) as supplementary publication numbers CCDC-264717 for $[Rb(18\text{-crown-}6)]_3As_7 \cdot 8\,NH_3$ (**2**) and CCDC-264718 for $(Ph_4P)_2CsAs_7 \cdot 5\,NH_3$ (**4**). Copies of the data can be obtained, free of charge, by application to the *CCDC*, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: data_request@ccdc.cam.ac.uk), or *via* the internet (http://www.ccdc.cam.ac.uk/products/csd/request).

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