Inorg. Chem. **2006**, *45*, 6723–6727

Inorganic Chemistry
Article

Dimers of Heptapnictide Anions: As_{14}^{4-} and P_{14}^{4-} in the Crystal Structures of $[Rb(18\text{-crown-}6)]_4As_{14}\cdot6NH_3$ and $[Li(NH_3)_4]_4P_{14}\cdot NH_3$

Tobias Hanauer, Jürgen C. Aschenbrenner, and Nikolaus Korber*

Institut für Anorganische Chemie der Universität Regensburg, Universitätsstrasse 31,
D-93053 Regensburg, Germany

Received March 10, 2006

Compounds $[Rb(18\text{-crown-}6)]_4As_{14}\cdot6NH_3$ (**1**) and $[Li(NH_3)_4]_4P_{14}\cdot NH_3$ (**2**) were prepared by the reaction of Rb_4As_6 with $SbPh_3$ and 18-crown-6 and by the reduction of white phosphorus with elemental lithium in liquid ammonia, respectively. Both were characterized by low-temperature single-crystal X-ray structure analysis. They were found to contain the C_i symmetrical Pn_{14}^{4-} anion (Pn = P, As), which consists of two nortricyclane-like Pn_7-cages connected by a single bond. Molecular complexes of $[Rb(18\text{-crown-}6)(NH_3)]_2[Rb(18\text{-crown-}6)]_2As_{14}$ are formed in **1**, which are connected to fanfold sheets via N–H···O bonds. The anion is isolated in **2**, and N–H···N bonds result in the formation of $\{[Li(NH_3)_4](\mu\text{-}NH_3)_2[Li(NH_3)_4]\}^{2+}$ cationic complexes.

Introduction

There are numerous examples of binary compounds between phosphorus or arsenic and alkali or alkaline earth metals, with the (poly)phosphides exceeding the (poly)arsenides in quantity by far. Nevertheless, many polyanion types are known both for arsenic and phosphorus. The most common molecular polyanions of phosphorus and arsenic certainly are the cage-structured nortricyclane[1] and trishomocubane[2] analogues, Pn_7^{3-} and Pn_{11}^{3-} species. These anions occur in compounds prepared by classical solid-state high-temperature reactions such as $M_3^IPn_7$ (M = Li−Cs)[3−9] or $M_3^IPn_{11}$ (M = K, Rb, Cs)[7,10,11] or in solvate crystals gained through extraction of these solids with solvents such as in $Cs_3As_7\cdot NH_3$, $[Rb(18\text{-crown-}6)]_3As_7\cdot8NH_3$, $Rb_3P_7\cdot7NH_3$, $Cs_3P_7\cdot3NH_3$, $Cs_3P_{11}\cdot3NH_3$, or $[Cs(18\text{-crown-}6)]_2CsAs_{11}\cdot8NH_3$.[12−16] Further possibilities are direct reduction of elemental arsenic or phosphorus with alkaline metals in liquid ammonia or the use of precursor materials, which results in compounds such as $Cs_3As_7\cdot6NH_3$, $[Li(NH_3)_4]_3As_7\cdot NH_3$, or $[Li(TMEDA)]_3As_7\cdot OEt_2$ and $[Li(DME)]_3As_7\cdot OEt_2$, $[Rb(18\text{-crown-}6)]_3P_7\cdot6NH_3$, or $[K(18\text{-crown-}6)]_3K_3(P_7)_2\cdot10NH_3$.[13,17−19] Substitution reactions using the polyanions as starting materials yielded derivative compounds such as $[PPh_4]_2HP_7\cdot3NH_3$, $[NBuMe_3]_2[HP_{11}]$, $[PPh_4][(PCH_2)P_7]$, $[K(2,2,2\text{-crypt})]_2[(PCH_2)As_7]$, $[P_{11}(SiMe_3)_3]$, or $[As_7(SiMe_3)_3]$.[20−23] While substantial progress has been made in the field of oligomeric anions based on

---

* To whom correspondence should be addressed. Fax: +49-941-9431812. E-mail: nikolaus.korber@chemie.uni-regensburg.de.

(1) von Ragué Schleyer, P. *J. Am. Chem. Soc.* **1958**, *80*, 1700−1704.
(2) Helmchen, G.; Staiger, G. *Angew. Chem.* **1977**, 119−120.
(3) Hönle, W.; Buresch, J.; Wolf, J.; Peters, K.; Chang, J. H.; von Schnering, H. G. *Z. Kristallogr.−New Cryst. Struct.* **2002**, *217*, 489−490.
(4) Hönle, W.; Buresch, J.; Peters, K.; Chang, J. H.; von Schnering, H. G. *Z. Kristallogr.−New Cryst. Struct.* **2002**, *217*, 487−488.
(5) Hönle, W.; Buresch, J.; Peters, K.; Chang, J. H.; von Schnering, H. G. *Z. Kristallogr.−New Cryst. Struct.* **2002**, *217*, 485−486.
(6) Emmerling, F.; Röhr, C. *Z. Naturforsch. B* **2002**, *57*, 963−975.
(7) von Schnering, H. G.; Hönle, W. *Chem. Rev.* **1988**, *88*, 243−273.
(8) Manriquez, V.; Hönle, W.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1986**, *539*, 95−109.
(9) Meyer, T.; Hönle, W.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1987**, *552*, 69−80.
(10) Emmerling, F.; Röhr, C. *Z. Anorg. Allg. Chem.* **2003**, *629*, 467−472.
(11) von Schnering, H. G.; Somer, M.; Kliche, G.; Hönle, W.; Meyer, T.; Wolf, J.; Ohse, L.; Kempa, P. B. *Z. Anorg. Allg. Chem.* **1991**, *601*, 13−30.
(12) Somer, M.; Hönle, W.; von Schnering, H. G. *Z. Naturforsch. B* **1989**, *44*, 296−306.
(13) Kraus, F.; Korber, N. *Chem.− Eur. J.* **2005**, *11*, 5945−5959.
(14) Korber, N.; Daniels, J. *Helv. Chim. Acta* **1996**, *79*, 2083−2087.
(15) Knettel, D.; Reil, M.; Korber, N. *Z. Naturforsch. B* **2001**, *56*, 965−969.
(16) Hanauer, T.; Korber, N. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1135−1140.
(17) Hanauer, T.; Grothe, M.; Reil, M.; Korber, N. *Helv. Chim. Acta* **2005**, *88*, 950−961.
(18) Driess, M.; Merz, K.; Pritzkow, H.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2507−2510.
(19) Hübler, K.; Becker, G. *Z. Anorg. Allg. Chem.* **1998**, *624*, 483−496.
(20) Aschenbrenner, J. C.; Korber, N. *Z. Anorg. Allg. Chem.* **2004**, *630*, 31−32.
(21) Korber, N.; Daniels, J.; von Schnering, H. G. *Angew. Chem., Int. Ed.* **1996**, *35*, 1107−1110.
(22) Mattamana, S. P.; Promprai, K.; Fettinger, J. C.; Eichhorn, B. W. *Inorg. Chem.* **1998**, *37*, 6222−6228.
(23) von Schnering, H. G.; Fenske, D.; Hönle, W.; Binnewies, M.; Peters, K. *Angew. Chem.* **1979**, *91*, 755−756.

10.1021/ic060418j CCC: $33.50

molecular anions of group 14, especially nonagermanides, in recent years, such oligomeric substructures derived from Pn$_7^{3-}$ or Pn$_{11}^{3-}$ are rare. [(Ge$_9$)$_2$]$^{6-}$ dimers,[24] [(Ge$_9$)$_3$]$^{6-}$ trimers,[25] [(Ge$_9$)$_4$]$^{8-}$ tetramers,[26] and $_1^{\infty}${[Ge$_9$]}$^{2-}$ polymers[27] have been prepared from isolated Ge$_9^{4-}$ anions.[24] On the other hand, only two Pn$_{22}^{4-}$ anions in (NEtMe$_3$)$_4$P$_{22}$•2 NH$_3$ [28] and [Rb(2,2,2-crypt)]As$_{22}$•4DMF[29] and one Pn$_{14}^{4-}$ anion in Na$_4$P$_{14}$•6en[30] are known in the literature. Other oligomeric or polymeric polyphosphides, such as P$_{21}^{3-}$,[31] formally a trimer of P$_7$, are more condensed structures.

During our investigations on Zintl anions in liquid ammonia, we obtained the As$_{14}^{4-}$ and P$_{14}^{4-}$ anions in the thermally unstable ammoniates [Rb(18-crown-6)]$_4$As$_{14}$•6NH$_3$ and [Li(NH$_3$)$_4$]$_4$P$_{14}$•NH$_3$, which we were able to characterize by low-temperature crystallographic techniques.

Experimental Section

General. All manipulations were performed under an Ar atmosphere or in high vacuum by means of standard Schlenk techniques. 18-crown-6 was purified by sublimation before use. Rb$_4$As$_6$ was prepared in an evacuated glass ampule following the documented procedure.[32]

[Rb(18-crown-6)]$_4$As$_{14}$•6NH$_3$ (1). Rb$_4$As$_6$ (0,031 g, 0.039 mmol) and SbPh$_3$ (0.014 g, 0.039 mmol) were placed into a Schlenk tube, together with an excess of 18-crown-6 (0.041 g. 0.156 mmol), and treated with anhydrous liquid ammonia (20 mL), which was condensed into the vessel at 238 K. The yellow/greenish mixture was stored at this temperature for several days, and the solution turned orange/red. After some weeks, red block-shaped crystals of **1** had formed with a yield (calculated with respect to arsenic) of about 70%. These crystals lose ammonia and decompose to a black solid at about 260 K. Without SbPh$_3$, the reaction yields an As$_7^{3-}$-containing product exclusively.

[Li(NH$_3$)$_4$]$_4$P$_{14}$•NH$_3$ (2). Elemental Li (0.053 g, 7.564 mmol) and white (or red) phosphorus (0.937 g, 30.251 mmol) were placed into a Schlenk tube, into which liquid ammonia (20 mL) was condensed at 238 K. The initial blue solution, stored at 238 K, turned orange/red within a day. After two weeks, dark red crystals of **2** had formed with almost quantitative yield. These crystals lose ammonia when they are warmed to about 280 K, yielding a brown powder. This decomposition product can be redisolved in ammonia, resulting in the formation of **2** in quantitative yield.

X-ray Crystallography. The air and moisture sensitive crystals of **1** and **2** were taken directly from the ammonia solution. Reflection data were collected on an IPDS instrument (STOE & Cie) with graphite-monochromated Mo Kα radiation at a temperature of 123(2) K. The two structures were solved by direct methods with SHELXS-97[33] and optimized by full-matrix least-squares refinement on F^2 with SHELXL-97.[34] The absorption was corrected with DELredABS from Platon.[35,36] 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. The N−H distances were restraint to a standard deviation of 0.1 in **1**. Details of the structure elucidations and refinements are summarized in Table 3.

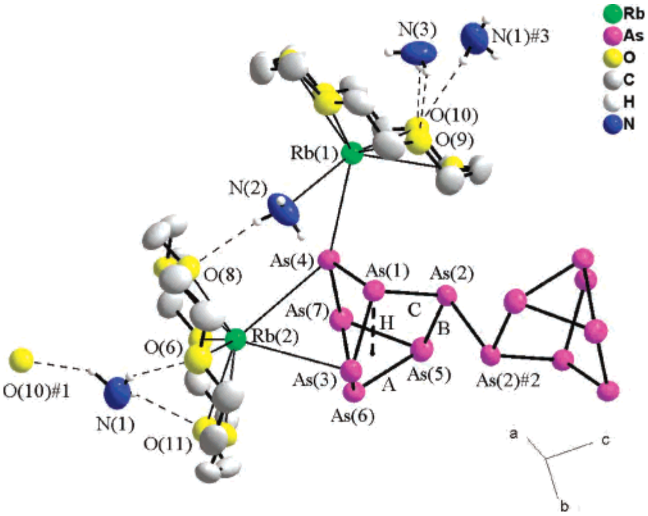

Figure 1. Detail of the structure of [Rb(18-crown-6)]$_4$As$_{14}$•6NH$_3$ (**1**) showing the central molecular complex and H bonds. The crown ether H atoms were omitted for clarity. Ellipsoids are drawn at the 70% probability level. Selected distances (in Å) and angles (in deg): As(2)−As(2)#1 = 2.4676(9), As(1)−As(3) = 2.3945(7), As(1)−As(4) = 2.4126(7), As(1)−As(2) = 2.4645(6), As(2)−As(5) = 2.4181(7), As(3)−As(6) = 2.3552(7), As(4)−As(7) = 2.3787(7), As(5)−As(6) = 2.4843(7), As(5)−As(7) = 2.4843(6), As(6)−As(7) = 2.5053(7), Rb(1)−As(4) = 3.5799(7), Rb(2)−As(3) = 3.5330(6), Rb(2)−As(4) = 3.6905(7), Rb(1)−N(1) = 3.010(5); As(5)−As(2)−As(2)#2 = 94.38(3), As(1)−As(2)−As(2)#2 = 100.87(3), As(3)−As(1)−As(4) = 105.55(2), As(3)−As(1)−As(2) = 102.68(2), As(4)−As(1)−As(2) = 93.56(2), As(5)−As(2)−As(1) = 100.02(2), As(6)−As(3)−As(1) = 99.00(2), As(7)−As(4)−As(1) = 99.71(2), As(2)−As(5)−As(6) = 105.16(2), As(2)−As(5)−As(7) = 99.45(2), As(3)−As(6)−As(5) = 106.24(2), As(3)−As(6)−As(7) = 108.03(2), As(4)−As(7)−As(5) = 106.27(2), As(4)−As(7)−As(6) = 104.42(2), As(6)−As(5)−As(7) = 60.56(2), As(5)−As(6)−As(7) = 59.72(2), As(5)−As(7)−As(6) = 59.72(2).

Results and Discussion

[Rb(18-crown-6)]$_4$As$_{14}$•6NH$_3$ (**1**) and [Li(NH$_3$)$_4$]$_4$P$_{14}$•NH$_3$ (**2**) were obtained either by the reaction of Rb$_4$As$_6$ with SbPh$_3$ in the presence of 18-crown-6 in liquid ammonia (**1**) or by direct reduction of white phosphorus with lithium in liquid ammonia (**2**). Both contain Pn$_{14}^{4-}$ (Pn = P, As) anions, which are dimers of the well-known nortricyclane-like Pn$_7^{3-}$ anions. While the P$_{14}^{4-}$ anion in **2** remains isolated and has no contacts to the metal cations, molecular complexes between As$_{14}^{4-}$, rubidium cations, crown ethers, and ammonia molecules are formed in **1**.

In **1**, the As$_{14}^{4-}$ anion (see Figure 1) is built up of only

---

(24) Suchentrunk, C.; Daniels, J.; Somer, M.; Carrillo-Cabrera, W.; Korber, N. *Z. Naturforsch. B* **2005**, *60*, 277−283.

(25) Yong, L.; Hoffmann, S. D.; Fässler, T. F. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1149−1153.

(26) Yong, L.; Hoffmann, S. D.; Fässler, T. F. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1977−1981.

(27) Downie, C.; Tang, Z.; Guloy, A. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 338−340.

(28) Korber, N. *Phosphorus, Sulfur Silicon Relat. Elem.* **1997**, *124−125*, 339−346.

(29) Haushalter, R.; Eichhorn, B. W.; Rheingold, A. L.; Geib, S. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1027−1028.

(30) von Schering, H. G. *Abstract of Papers*, 29th IUPAC Congress, Köln, Germany, 5−10 June, 1983; International Union of Pure and Applied Chemistry: Research Triangle Park, NC, **1983**; 36.

(31) Fritz, G.; Schneider, H. W.; Hönle, W.; von Schnering, H. G. *Z. Naturforsch. B* **1988**, *43*, 561−566.

(32) Hönle, W.; Krogull, G.; Peters, K.; von Schnering, H. G. *Z. Kristallogr.−New Cryst. Struct.* **1999**, *214*, 17−18.

(33) Sheldrick, G. M. *SHELXS-97*; Universiy of Göttingen: Göttingen, Germany, 1997.

(34) Sheldrick, G. M. *SHELXL-97*; Universiy of Göttingen: Göttingen, Germany, 1997.

(35) Spek, A. L. *PLATON−A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2003.

(36) Walker, N.; Stuart, D. *Acta Crystallogr. A* **1983**, *39*, 158−166.

Table 1. Characteristic Structural Features of the As_{14}^{4-} and P_{14}^{4-} Anions in Compounds **1** and **2**

	1	**2**
A_m (Å)	2.491	2.25
B_m (Å)	2.384	2.15
C_m (Å)	2.424	2.18
δ_m (deg)	100.6	101.1
γ_m (deg)	99.6	99.2
β_m (deg)	104.9	105.0
H (Å)	3.3728(8)	3.026(2)
$Q = H/A_m$	1.35	1.34

Table 2. Hydrogen Bonds with Proton Donor···Acceptor Distances (in Å) and Angles (in deg) in **1** and **2**[a]

	d(D−H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (deg)	D−H···A
1	0.97(6)	2.38(6)	3.222(6)	145(6)	N(1)−H(1AN)···O(10)#1
1	0.84(6)	2.65(6)	3.413(8)	152(7)	N(1)−H(1BN)···O(6)
1	0.86(6)	2.73(7)	3.480(7)	147(8)	N(1)−H(1CN)···O(11)
1	0.78(6)	2.69(7)	3.457(6)	168(9)	N(3)−H(3CN)···O(10)
1	0.86(5)	2.49(6)	3.293(7)	156(6)	N(3)−H(3AN)···O(9)
1	0.81(6)	2.46(6)	3.268(7)	171(5)	N(2)−H(2BN)···O(8)
2	0.91	2.59	3.316(6)	137.4	N(1)#2−H(1A)#2···N(9)
2	0.91	2.39	3.291(7)	168.6	N(4)#4−H(4A)#4···N(9)

[a] Symmetry operations: #1 $x, -y + 0.5, z - 0.5$; #2 $-x + 1, -y + 1, -z + 2$; #4 $x, y + 1, z$.

seven crystallographically independent arsenic atoms. The center of the bond linking the two As_7 monomers is situated on a crystallographic inversion center (2*b* of monoclinic space group $P2_1/c$), which completes the anion by symmetry. The characteristic structural features of the As_{14}^{4-} anion are listed in Table 1. Each As_7 anionic fragment is coordinated by two rubidium cations. Rb(2) coordinates η^2 at the formally negatively charged arsenic atoms As(3) and As(4) with distances of 3.5330(6) and 3.6905(7) Å, while Rb(1) has only one contact to the anion at As(4) at a distance of 3.5799(7) Å. These distances agree well with those found for the coordination of Rb^+ with monomeric As_7^{3-} in $[Rb(18\text{-crown-}6)]_3As_7\cdot 8NH_3$.[17] Each cation is also coordinated by the six oxygen atoms of the 18-crown-6 molecules with Rb−O distances of 2.896(3)−3.171(3) Å. This coordination between the cations and the crown ether ligands displays the usual eccentricity, where the cations are not located in the center of the crown ether but are situated above the plane defined by the six oxygen atoms of each crown ether molecule by 1.183(1) (Rb(1)) and 1.148(1) Å (Rb(2)), which is also very similar to the situation in $[Rb(18\text{-crown-}6)]_3As_7\cdot 8NH_3$. Ammonia molecule N(2) completes the coordination sphere of Rb(1), which results in the neutral molecular complex $[Rb(18\text{-crown-}6)(NH_3)]_2[Rb(18\text{-crown-}6)]_2As_{14}$. N(2) and two additional ammonia molecules (N(1) and N(3)) are bound to the crown ether molecules via N−H···O hydrogen bonds (see Table 2); the H···O distances are shorter than the sum of the van der Waals radii by up to 12.5%. Thus, the molecular units are connected by hydrogen bonds to fanfold sheets parallel to the crystallographic *ac* plane and are stacked along the *b* axis, which is shown in Figure 2.

The center of the P_{14}^{4-} anion (see Figure 3) in **2** is also located on a center of symmetry (1*h* of triclinic space group $P\bar{1}$), and consequently, the anion is also built up by only seven crystallographic independent atoms. The characteristic structural features of the P_{14}^{4-} anion are listed in Table 1.

Table 3. Crystallographic Data for **1** and **2**

	1	**2**
structural formula	$[Rb(18\text{-crown-}6)]_4As_{14}\cdot 6NH_3$	$[Li(NH_3)_4]_4P_{14}\cdot NH_3$
empirical formula	$C_{48}H_{114}As_{14}N_6O_{24}Rb_4$	$H_{54}Li_4N_{18}P_{14}$
M_r (g mol^{-1})	2550.21	767.95
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	10.415(1)	9.283(3)
b (Å)	17.291(1)	9.508(3)
c (Å)	25.573(2)	13.466(4)
α (deg)	90	99.24(3)
β (deg)	100.64(1)	91.66(3)
γ (deg)	90	118.45(3)
V (Å^3)	4526.2(6)	1023.8(6)
Z	2	1
ρ_c (g cm^{-3})	1.871	1.246
μ (mm^{-1})	7.291	0.599
$F(000)$	2492	402
θ range (deg)	2.00−25.96	2.51−23.26
h, k, l ranges	−12−12, −21−21, −31−31	−10−10, −10−10, −14−14
all, indpendent reflns	41 318, 8803	5987, 2785
R_{int}	0.0643	0.0674
completeness to θ (%)	99.4	94.6
no. of params, restraints	493, 6	175, 0
S (all data)	0.806	0.934
$R_1(I > 2\sigma I)$, R_1(all data)	0.0284, 0.0541	0.0409, 0.0568
$R_2(I > 2\sigma I)$, R_2 (all data)	0.0529, 0.0564	0.1006, 0.1050
$\Delta\rho_{max}/\Delta\rho_{min}$ (e/Å^3)	0.452/−0.413	0.693/−0.434

In contrast to compound **1**, no coordinating contacts between the anion and metal cations are observed. Instead, **2** is built from tetraammine lithium complexes $[Li(NH_3)]_4^+$ of approximately tetrahedral shape with Li−N distances of 2.048(8)−2.083(7) Å and angles of 104.7(3)−119.2(4)° and isolated P_{14}^{4-} anions. While the $[Li(NH_3)]_4^+$ complexes of Li(2) show no further bonding contacts, hydrogen bonds (see Table 2) to ammonia molecule N(9) result in $\{[Li(NH_3)_4]$-

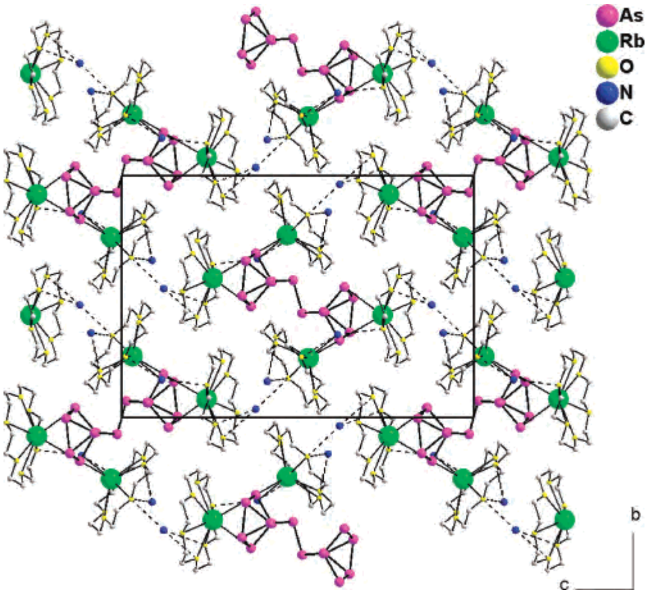

Figure 2. Projection of the structure of $[Rb(18\text{-crown-}6)]_4As_{14}\cdot 6NH_3$ (**1**) on the *bc* plane. H atoms are omitted for clarity. The hydrogen bridges are shown as dotted lines between the N and O atoms.

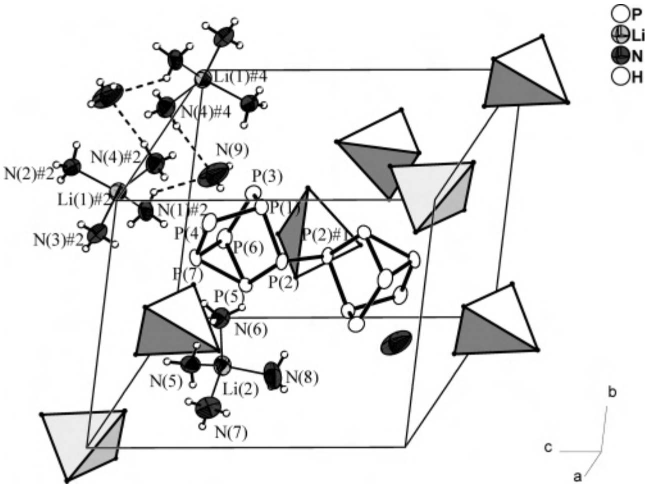

Figure 3. View of the structure of $[Li(NH_3)_4]P_{14}{\cdot}NH_3$ (**2**). The $[Li(NH_3)_4]^+$ complexes are partly shown as polyhedra without hydrogen atoms. Ellipsoids are drawn at the 70% probability level. Selected distances (in Å) and angles (in deg): P(2)−P(2)#1 = 2.230(2), P(1)−P(2) = 2.214(2), P(1)−P(3) = 2.151(2), P(1)−P(4) = 2.176(2), P(2)−P(5) = 2.191(2), P(3)−P(6) = 2.122(2), P(4)−P(7) = 2.142(2), P(5)−P(7) = 2.244(2), P(5)−P(6) = 2.250(2), P(6)−P(7) = 2.251(2); P(5)−P(2)−P(2)#1 = 96.05(7), P(1)−P(2)−P(2)#1 = 101.32(8), P(3)−P(1)−P(4) = 104.74(6), P(3)−P(1)−P(2) = 104.30(7), P(4)−P(1)−P(2) = 94.20(7), P(5)−P(2)−P(1) = 100.27(6), P(6)−P(3)−P(1) = 98.93(6), P(7)−P(4)−P(1) = 98.43(7), P(2)−P(5)−P(7) = 98.60(6), P(2)−P(5)−P(6) = 104.18(6), P(3)−P(6)−P(5) = 107.84(6), P(3)−P(6)−P(7) = 106.29(7), P(4)−P(7)−P(5) = 107.38(6), P(4)−P(7)−P(6) = 105.72(6), P(7)−P(5)−P(6) = 60.13(5), P(5)−P(6)−P(7) = 59.83(6), P(5)−P(7)−P(6) = 60.05(6).

$(\mu\text{-}NH_3)_2[Li(NH_3)_4]\}^{2+}$ dimers for Li(1). These hydrogen bonds are shorter the sum of the van der Waals radii by about 6 and 13%, which is typical for N−H···N hydrogen bonds in ammoniates.[37] Such homoleptic $[Li(NH_3)_4]^+$ complexes are the dominating cations in lithium-containing ammoniates, such as $[Li(NH_3)_4]_3As_7{\cdot}NH_3$[17] or $[Li(NH_3)_4]_3P_{11}{\cdot}5NH_3$,[38] whereas direct coordination of Li^+ to polyanionic clusters is rare. A similar cationic complex dimer, in this case $\{[Li(NH_3)_4](\mu\text{-}NH_3)[Li(NH_3)_4]\}^{2+}$, can be found in $[Li(NH_3)_4]_3As_7{\cdot}NH_3$, while in $[Li(NH_3)_4]_3P_{11}{\cdot}5NH_3$, all tetraammine complexes are connected by a complicated network of N···H−N hydrogen bonds. This cationic complex is also very similar to the $\{[NH_4(NH_3)_4](\mu\text{-}NH_3)[NH_4(NH_3)_4]\}^{2+}$ complex in $[NH_4(NH_3)_4][BPh_4]{\cdot}NH_3$.[37]

Both dimeric anions As_{14}^{4-} and P_{14}^{4-} differ from the monomeric Pn_7^{3-} with respect to the details for the cage bond lengths, which is caused by the additional connecting bond between the two monomers. In an ideal case, the Pn_7^{3-} anions have C_{3v} symmetry, and the bonding distances in all ionic nortricyclanes show a characteristic distribution of three types of bonds, with $A > C > B$ (see Figure 1). The ratio $Q = H/A_m$, where H is the height of the anion and A_m is the mean value of distances A, typically lies between 1.31 and 1.35 for ionic systems, in contrast to 1.42 for neutral, covalently substituted cages with $A > B > C$. Additionally, the angles δ (at the apical atom between to bonds of type C), γ (at the divalent atoms between bonds of type C and B), and β (at the basal atoms between bonds of type B and A) show a different distribution with $\beta > \delta > \gamma$ for ionic species and $\beta > \gamma > \delta$ for neutral ones.[7]

In the As_{14}^{4-} and P_{14}^{4-} anions, the connecting bond length (As(2)−As(2)#1, P(2)−P(2)#1) are 2.4676(9)/ and 2.230(2) Å, which are significantly shorter than the bonds in the triangular base of Pn_7^{3-} anions with mean values, A_m, of 2.52 and 2.27 Å. In contrast, this value shows good agreement with the distances between trivalent apical and trivalent equatorial pnictide atoms (2.46 and 2.23 Å) in Pn_{11}^{3-} anions,[10,11,15,16,38] which is probably the result of the similar bonding angles. These angles are about 60° within the triangular base of Pn_7^{3-} anions, but they are 94.38(3) and 100.87(3)° at As(2) (96.05(7) and 101.32(8)° at P(2) in the new compounds, which is similar to the angles of 99−106° in As_{11}^{3-} anions or 101−105° in P_{11}^{3-} anions. The bonding distances between the apical atoms, As(1)/P(1), and the equatorial atoms, As(2)/P(2), As(3)/P(3), and As(4)/P(4), show strong variation. Where As(1)−As(3)/P(1)−P(3) and As(1)−As(4)/P(1)−P(4) show only slight differences (2.3945(7) and 2.4126(7)/2.151(2) and 2.176(2) Å), As(1)−As(2)/P(1)−P(2) is elongated to 2.4645(6)/2.214(2) Å. This value is virtual the same as that for As(2)−As(2)#1/P(2)−P(2)#1, which impressively demonstrates the fundamental proportional correlation between valence and bonding lengths. The same holds true for the bonds of type B between the equatorial and the basal pnictide atoms with bond lengths of 2.4181(7)/2.191(2), 2.3552(7)/2.122(2), and 2.3787(7)/2.142(2) Å. The mean values of A, B, and C (2.491/2.25, 2.384/2.15, and 2.424/2.18 Å) show only a weak tendency to shift from $A > C > B$ to $A > B > C$, since only B increases slightly from 2.36/2.13 (Pn_7^{3-}) to 2.38/2.15 Å. A small decrease of the bond lengths within the triangular base to a mean value of $A_m = 2.491/2.25$ Å fits well with the observations made in the systems Pn_7^{3-} ($A_m = 2.52/2.27$ Å), HP_7^{2-}(2.24 Å), $Pn_7R_2^-$ ($A_m = 2.44/2.22$ Å),[22] and Pn_7R_3 ($A_m = 2.44/2.22$ Å). Furthermore, the height of the cages, H, increases to 3.3728(8)/3.026(2) Å (3.337/2.99 Å for Pn_7^{3-}), which results in Q values of 1.35/1.34.

The compression of the angles As(4)−As(1)−As(2)/P(4)−P(1)−P(2) (93.56(2)/ 94.20(7)°) and As(2)−As(5)−As(7)/P(2)−P(5)−P(7) (99.45(2)/ 98.60(6)°) is probably caused by the steric demand of the second Pn_7 fragment and is also observed in $Pn_7R_2^-$ anions.

While the As_{14}^{4-} anion in **1** is, to our knowledge, a completely new polyarsenide anion, P_{14}^{4-} has already been mentioned once in the literature as the anion in the solvate compound $Na_4P_{14}{\cdot}6en$.[30] Unfortunately, no structural data for this compound are available, so no direct comparison could be made.

Our results indicate that a more understood chemistry of polypnictide anions using cage anions as building blocks should be possible, comparable to the recent successes in group 14 chemistry with the Ge_9 cages mentioned above. Especially interesting is the question of whether infinitely extended polypnictides, which are known to form in high-temperature solid-state reactions, may also be prepared in solution at low temperatures using similar techniques.

---

(37) Rossmeier, T.; Reil, M.; Korber, N. *Inorg. Chem.* **2004**, *43*, 2206−2212.

(38) Korber, N.; Richter, F. *J. Chem. Soc., Chem. Commun.* **1996**, 2023−2024.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft DFG and the Fonds der chemischen Industrie.

Supporting Information Available: Crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 297275. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax, int. code + (1223)336-033; e-mail for inquiry, fileserver@ccdc.cam.ac.uk; e-mail for deposition, deposit@ccdc.cam.ac.uk). Further details of the crystal structure investigations for **2** are available on request from the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen with the deposition number CSD-416230.

IC060418J