

Nature of the Chemical Bond in Polypnictides: The Lone Pair Aromatic Anions P_4^{2-} and As_4^{2-}

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Received August 24, 2005

The nature of the chemical bond in inorganic 6π aromatic systems such as P_4^{2-} , S_4^{2+} , or S_2N_2 is a matter of particular interest because the phenomenon of aromaticity is not as well established in these compounds as it is in the classic aromatic hydrocarbons. Here we present the synthesis, NMR spectra, and crystal structures of bis-(potassium(18-crown-6))cyclo-tetraphosphide-ammonia(1/2) ($K@18\text{-crown-6})_2P_4 \cdot 2NH_3$, bis(rubidium(18-crown-6))cyclo-tetraphosphide-cyclo-tetraarsenide-ammonia(1/3) ($Rb@18\text{-crown-6})_2(P_4)_{0.85}(As_4)_{0.15} \cdot 3NH_3$, both containing the 6π aromatic cyclo-tetraphosphide anion, P_4^{2-} , and the synthesis and crystal structure of bis(potassium(18-crown-6))cyclo-tetraarsenide ($K@18\text{-crown-6})_2As_4$. As a common motive, all three compounds feature neutral molecules with a triple-decker-like coordination of the cyclo-tetrapnictide anion between two crown ether-coordinated alkali metal cations. With ab initio calculations on the HF level and by employing the concept of the electron localization function ELF, we established that the cyclo-tetraarsenide anion, As_4^{2-} , shows electron delocalization primarily through the lone pairs, as does P_4^{2-} , and may consequently also be described as lone pair aromatic.

Introduction

With the synthesis of dicesium cyclo-tetraphosphide-ammonia(1/2) $Cs_2P_4 \cdot 2NH_3$,^{1,2} the 6π aromatic P_4^{2-} anion, the lighter congener of the hitherto known E_4^{2-} anions ($E = As,^3 Sb,^4 Bi^5$) and the missing isoelectronic partner of the 6π aromatic S_4^{2+} cation, was found.^{6–12} The synthesis and crystal structures of bis(potassium(18-crown-6))cyclo-tetraphosphide-ammonia(1/2) ($K@18\text{-crown-6})_2P_4 \cdot 2NH_3$ (**1**), bis(rubidium(18-crown-6))cyclo-tetraphosphide-cyclo-tetraarse-

nide-ammonia(1/3) ($Rb@18\text{-crown-6})_2(P_4)_{0.85}(As_4)_{0.15} \cdot 3NH_3$ (**2**), and bis(potassium(18-crown-6))cyclo-tetraarsenide ($K@18\text{-crown-6})_2As_4$ (**3**) are reported here, together with the NMR data of **1** and **2**. The electron localization function, ELF,^{13–23} was employed to show that the aromaticity in P_4^{2-} , S_4^{2+} , and P_5^- differs from that in the classic aromatic hydrocarbons, and the term “lone pair aromaticity” was proposed for this behavior.²⁴ Now we set out to show that this concept can also be expanded to the heavier congener of P_4^{2-} , the cyclo-tetraarsenide dianion, As_4^{2-} , which is also lone pair aromatic within the ELF concept.^{17,19}

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Results and Discussion

In our first encounter with the P_4^{2-} anion in the compound $Cs_2P_4 \cdot 2NH_3$,^{1,2} the cyclotetraphosphide anion was coordinated by a total of eight symmetry equivalent cesium cations, which brought up the question of its stability as a molecular moiety outside of this more or less solid-state-like environment and outside organometallic complexes.^{1,2} This is not an absurd question since the related molecular P_6^{4-} anion has up to now only been synthesized in the solid state as M_4P_6 ($M = K, Rb, Cs$) and in some organometallic complexes,^{25–33} and so far no one has been able to obtain isolated P_6^{4-} anions, either in a nonbinary compound or in solution. Furthermore, we were not able to find a ground-state geometry with ab initio calculations for the P_6^{4-} anion in the point groups D_{6h} , D_{3d} , D_{3h} , D_{2h} , and C_{2v} ; we obtained transition states only with geometries close to D_{6h} . The same is unfortunately true for the $K_2P_6^{2-}$ anion in an idealized D_{6h} symmetry, and even in point group C_s , we only obtained a first-order transition state. The D_{2h} symmetry of $K_2P_6^{2-}$ present in the crystal structure is a ground state. Finally, we found a twist-like conformation to be a ground state for P_6^{4-} . However, the possibility of P_6^{4-} persisting in solution or existing outside the situations mentioned above still seems to be elusive. The situation with the cyclotetraphosphide anion P_4^{2-} is different as the ground state geometries are easily obtained in point group D_{4h} , and they are also obtained for the D_{4h} symmetric M_2P_4 ($M = Na, K, Rb, Cs$) species.^{1,2,34} Furthermore, the existence of the cyclotetraphosphide anion in solution was shown.^{1,2} Now we are able to synthesize discrete molecular entities containing the cyclotetraphosphide anion in compounds **1** and **2**, thereby proving the existence of ionic P_4^{2-} outside a solid-state-like environment, as in $Cs_2P_4 \cdot 2NH_3$. In the case of As_4^{2-} and K_2As_4 , ab initio calculations also shown the point group D_{4h} to be a ground state, and we synthesized a variety of compounds of which compound **3** is reported below.³⁵

Structure of Bis(potassium(18-crown-6))cyclotetraphosphide-ammonia(1/8.5) ($K@18\text{-crown-6}$) $_2P_4 \cdot 8.5NH_3$ (1**).** The compound was synthesized from K_4P_2I ³⁶ using lithium

and 18-crown-6 in a liquid ammonia solution. As the anionic moiety of this structure, the recently discovered 6π aromatic P_4^{2-} anion is present.^{1,2} The phosphorus–phosphorus bond lengths of 2.167(2) [P(1)–P(2)], 2.161(2) [P(2)–P(3)], 2.172(2) [P(3)–P(4)], and 2.160(2) Å [P(4)–P(1)] are very similar to each other. The P–P–P angles are close to 90° with P(4)–P(1)–P(2) = 90.32(8)°, P(3)–P(2)–P(1) = 89.81(9)°, P(2)–P(3)–P(4) = 90.16(9)°, and P(1)–P(4)–P(3) = 89.71(8)°. The torsion angle P(1)–P(2)–P(3)–P(4) shows a slight bending with 0.54(11)°. Thus, the P_4^{2-} anion in **1** is almost square planar. It is coordinated in an η^4 -like manner by two potassium cations, K(1) and K(2), which are located 3.058(2) and 3.101(2) Å above and below a least-squares plane defined by the phosphorus atoms of the P_4^{2-} molecule. The potassium cations are not directly above the ring center but are shifted approximately 0.2 Å toward the P(1)–P(2) bond. The phosphorus–potassium distances are available in the caption of Figure 1. Since both potassium ions are coordinated by P_4^{2-} and by a molecule of 18-crown-6, their coordination number is ten. The K–O bond lengths are in the range of 2.804(4)–3.162(5) Å. Potassium ion K(1) is 1.057(3) Å away from a least-squares plane defined by the oxygen atoms of its crown ether molecule; K(2) is just 0.860(3) Å away from its corresponding least-squares plane. This difference is easily understood, as a molecule of ammonia is attached to the other side of the crown ether molecule of potassium ion K(1) by N–H···O hydrogen bonding with the nitrogen atom N(1) lying only 2.13(1) Å away from the above-mentioned least-squares plane. A very similar hydrogen-bonded crown ether–ammonia complex was recently described in 18-crown-6(NH_3)₂.³⁷ Hydrogen bond lengths and angles are found in the caption of Figure 1. A molecule of ammonia of crystallization is located about 4.5 Å away from the phosphorus ring center. Unfortunately, we were not able to locate the hydrogen atoms attached to nitrogen atom N(2). The described moiety of $(K@18\text{-crown-6})_2P_2 \cdot 2NH_3$ is shown on the left side of Figure 1. These entities are interlocked along the crystallographic c axis; the crown ethers are facing into the voids around the P_4^{2-} anions (Figure 1, right side). The other ammonia molecules of crystallization with nitrogen atoms N(3)–N(11) are found to be heavily disordered in channels running parallel to the crystallographic a axis (Figure 1, right). The assignment of hydrogen atoms to them is of course a futile task. Crystallographic details are available in Table 1.

The $^{31}P\{^1H\}$ -NMR spectrum of the liquid ammonia solution of the reaction mixture at -40 °C shows a variety of signals of which the singlet at 322.8 ppm indicates the presence of the 6π aromatic P_4^{2-} anion. This signal is also a singlet in the ^{31}P NMR spectrum. The signal at -268.9 ppm which is a singlet in the $^{31}P\{^1H\}$ -NMR spectrum and a triplet with $^1J_{P,H} = 140$ Hz in the ^{31}P NMR spectrum belongs to PH_2^- , which is encountered quite often in our liquid ammonia solutions.^{1,2,24} The chemical shift of the P_4^{2-} anion is dependent on the counterion, as was pointed out previously, and is in good agreement with the findings there.^{1,2,24,28}

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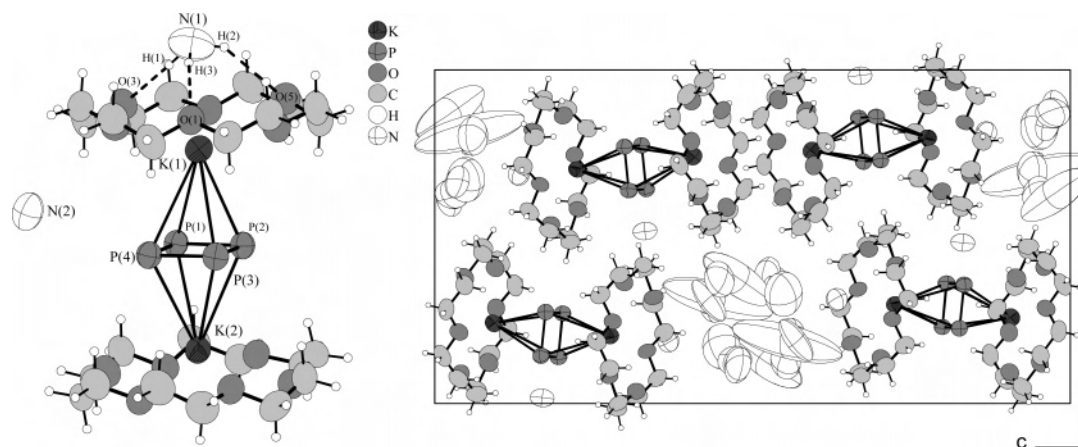


Figure 1. Projection of the $(\text{K@18-crown-6})_2\text{P}_4 \cdot 2\text{NH}_3$ unit (left) and a projection of the unit cell on the bc plane. Dashed bonds indicate $\text{N-H}\cdots\text{O}$ hydrogen bonding. Thermal ellipsoids are drawn at the 70% probability level. Selected bond lengths (\AA) and angles (deg): $\text{K}(1)\text{--P}(1) = 3.398(2)$, $\text{K}(1)\text{--P}(2) = 3.320(2)$, $\text{K}(1)\text{--P}(3) = 3.449(2)$, $\text{K}(1)\text{--P}(4) = 3.547(2)$, $\text{K}(2)\text{--P}(1) = 3.342(2)$, $\text{K}(2)\text{--P}(2) = 3.439(2)$, $\text{K}(2)\text{--P}(3) = 3.603(2)$, $\text{K}(2)\text{--P}(4) = 3.498(2)$. Hydrogen bond lengths (\AA) and angles (deg) (D = donor, A = acceptor): $\text{N}(1)\text{--H}(3)\cdots\text{O}(1)$ D–H = 1.00(7), $\text{H}\cdots\text{A} = 2.39(7)$, $\text{D}\cdots\text{A} = 3.368(9)$, $\angle\text{DHA} = 167(11)$; $\text{N}(1)\text{--H}(1)\cdots\text{O}(3)$ D–H = 1.00(7), $\text{H}\cdots\text{A} = 2.35(7)$, $\text{D}\cdots\text{A} = 3.31(1)$, $\angle\text{DHA} = 163(11)$; $\text{N}(1)\text{--H}(2)\cdots\text{O}(5)$ D–H = 1.00(7), $\text{H}\cdots\text{A} = 2.7(1)$, $\text{D}\cdots\text{A} = 3.54(1)$, $\angle\text{DHA} = 140(11)$.

Table 1. Crystallographic Data of the Presented Structures

	1	2	3
empirical formula	$\text{C}_{24}\text{H}_{73.35}\text{K}_2\text{N}_{8.45}\text{O}_{12}\text{P}_4$	$\text{C}_{24}\text{H}_{57}\text{As}_{0.6}\text{N}_{3.0}\text{O}_{12}\text{P}_{3.4}\text{Rb}_2$	$\text{C}_{24}\text{H}_{48}\text{As}_4\text{K}_2\text{O}_{12}$
mol mass (g/mol)	874.64	900.92	906.52
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
a (\AA)	8.742(1)	8.639(1)	9.9917(7)
b (\AA)	16.402(2)	16.516(2)	9.890(1)
c (\AA)	31.321(3)	28.540(4)	18.695(1)
β (deg)	90	95.07(2)	96.004(8)
V (\AA^3)	4491.0(9)	4056.2(9)	1837.3(2)
Z	4	4	2
ρ_{calcd} (Mg/m^3)	1.287	1.475	1.639
T (K)	123	123	123
$F(000)$	1882	1851	916
μ (Mo $\text{K}\alpha$) (mm^{-1})	0.411	3.085	3.884
θ range (deg)	2.31–25.00	2.47–25.00	2.33–28.05
measured, independent, and observed ($I > 2\sigma(I)$) reflns	29384, 7806, 4348	26286, 7145, 3373	16248, 4264, 3322
R_{int}	0.1609	0.1087	0.0431
h, k, l range	–10/10, –19/19, –36/34	–10/10, –19/19, –33/33	–12/13, –13/13, –24/21
$R(F)$ ($I > 2\sigma(I)$, all data)	0.0532, 0.1010	0.0477, 0.1211	0.0280, 0.0384
$wR(F^2)$ ($I > 2\sigma(I)$, all data)	0.1134, 0.1323	0.0889, 0.1058	0.0671, 0.6950
S (all data)	0.847	0.792	0.920
data, params, restraints	7806, 491, 3	7145, 468, 13	4264, 202, 0
$(\Delta/\sigma)_{\text{max}}$	0.494	0.001	0.001
$\Delta\rho_{\text{max}}$ [$\text{e}\text{\AA}^{-3}$]	0.379	0.482	1.248
$\Delta\rho_{\text{min}}$ [$\text{e}\text{\AA}^{-3}$]	–0.419	–0.634	–0.350
Flack parameter x	–0.06(8)	–	–

The other signals present in the NMR spectra are from a (hydrogen)polyphosphide that we are not able to identify yet.

Structure of Bis(rubidium(18-crown-6)cyclotetraphosphide-cyclotetraarsenide-ammonia(1/3) (Rb@18-crown-6) $_2(\text{P}_4)_{0.85}(\text{As}_4)_{0.15} \cdot 3\text{NH}_3$ (2). This compound was synthesized from rubidium arsenide(4/6) Rb_4As_6 ³⁸ and postassium phosphide(4/6) K_4P_6 ^{27,29} using 18-crown-6 in a liquid ammonia solution. All atoms of the structure reside on the common $4e$ position of the space group $P2_1/n$. The 6π aromatic cyclotetraphosphide anion P_4^{2-} and the As_4^{2-} anion are present as the anionic moieties since they partially occupy the same site in a ratio of 85/15. For the sake of simplicity, we will only talk about the phosphorus atoms when referring

to this structure. The P_4^{2-} anion shows nearly equivalent phosphorus–phosphorus bond lengths of 2.212(3) \AA for $\text{P}(1)\text{--P}(2)$, 2.213(3) \AA for $\text{P}(1)\text{--P}(4)$ and $\text{P}(2)\text{--P}(3)$, and 2.209(3) \AA for $\text{P}(3)\text{--P}(4)$ (Figure 2). Because of the partial site occupation with As_4^{2-} , the bond lengths are of course longer than in **1**. The P--P--P bond angles of the four-membered ring are equal within the standard deviation with $\text{P}(1)\text{--P}(2)\text{--P}(3) = 89.91(9)^\circ$, $\text{P}(2)\text{--P}(1)\text{--P}(4) = 90.01(10)^\circ$, $\text{P}(4)\text{--P}(3)\text{--P}(2) = 90.09(10)^\circ$, and $\text{P}(3)\text{--P}(4)\text{--P}(1) = 89.98(9)^\circ$, forming a square. With a torsion angle of $-0.42(10)^\circ$, the square is almost planar. The P_4^{2-} anion is coordinated by two rubidium cations in an η^4 -like fashion with $\text{Rb}(1)$ and $\text{Rb}(2)$ being 3.258(2) and 3.207(2) \AA above and below, respectively, a least-squares plane through the phosphorus atoms. The rubidium ions are shifted ap-

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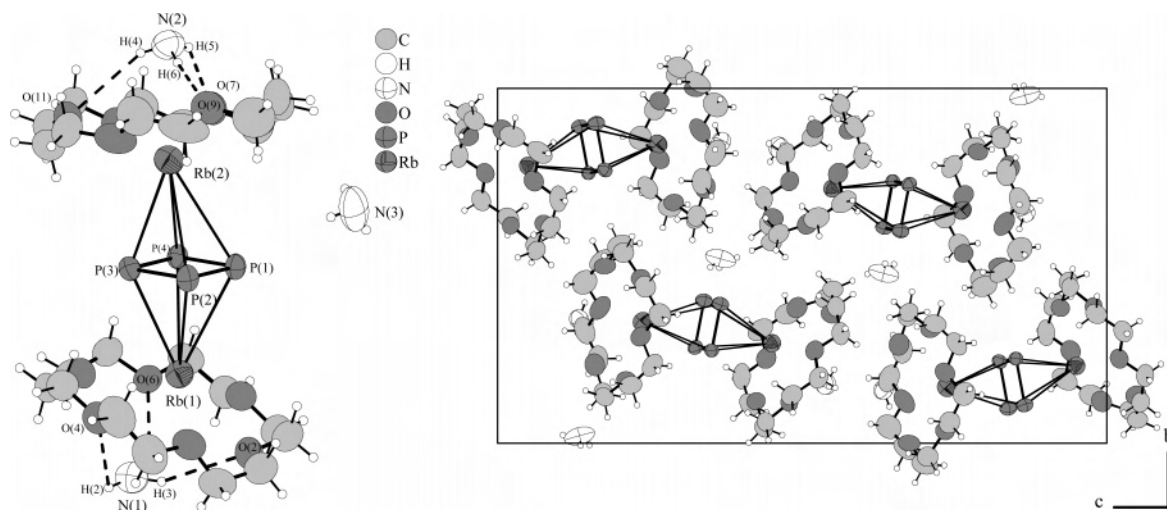


Figure 2. Projection of the $(\text{Rb}@18\text{-crown-6}(\text{NH}_3)_2(\text{P}_4)_{0.85}(\text{As}_4)_{0.15})$ molecule with a molecule of ammonia of crystallization (left) and a projection of the unit cell on the bc plane (right). Dashed bonds indicate $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonding. Thermal ellipsoids are drawn at the 70% probability level. Selected bond lengths (\AA) and angles (deg): $\text{P}(1)-\text{P}(2) = 2.212(3)$, $\text{P}(1)-\text{P}(4) = 2.213(3)$, $\text{P}(2)-\text{P}(3) = 2.213(3)$, $\text{P}(3)-\text{P}(4) = 2.209(3)$, $\text{P}(1)-\text{P}(2)-\text{P}(3) = 89.91(9)$, $\text{P}(2)-\text{P}(1)-\text{P}(4) = 90.01(10)$, $\text{P}(4)-\text{P}(3)-\text{P}(2) = 90.09(10)$, $\text{P}(3)-\text{P}(4)-\text{P}(1) = 89.98(9)$, $\text{Rb}(1)-\text{P}(1) = 3.647(2)$, $\text{Rb}(1)-\text{P}(2) = 3.751(2)$, $\text{Rb}(1)-\text{P}(3) = 3.597(2)$, $\text{Rb}(1)-\text{P}(4) = 3.504(2)$, $\text{Rb}(2)-\text{P}(1) = 3.761(2)$, $\text{Rb}(2)-\text{P}(2) = 3.652(2)$, $\text{Rb}(2)-\text{P}(3) = 3.422(2)$, $\text{Rb}(2)-\text{P}(4) = 3.525(2)$. Hydrogen bond lengths (\AA) and angles (deg) ($\text{D} = \text{donor}$, $\text{A} = \text{acceptor}$): $\text{N}(2)-\text{H}(6)\cdots\text{O}(9)$ $\text{D}-\text{H} = 1.03(8)$, $\text{H}\cdots\text{A} = 2.26(8)$, $\text{D}\cdots\text{A} = 3.279(10)$, $\angle\text{DHA} = 170(11)$; $\text{N}(2)-\text{H}(4)\cdots\text{O}(11)$ $\text{D}-\text{H} = 0.85(7)$, $\text{H}\cdots\text{A} = 2.85(7)$, $\text{D}\cdots\text{A} = 3.636(11)$, $\angle\text{DHA} = 154(7)$; $\text{N}(2)-\text{H}(5)\cdots\text{O}(7)$ $\text{D}-\text{H} = 0.99(9)$, $\text{H}\cdots\text{A} = 2.48(12)$, $\text{D}\cdots\text{A} = 3.276(11)$, $\angle\text{DHA} = 137(12)$; $\text{N}(1)-\text{H}(3)\cdots\text{O}(2)$ $\text{D}-\text{H} = 0.89(7)$, $\text{H}\cdots\text{A} = 2.90(8)$, $\text{D}\cdots\text{A} = 3.692(11)$, $\angle\text{DHA} = 148(8)$; $\text{N}(1)-\text{H}(2)\cdots\text{O}(4)$ $\text{D}-\text{H} = 0.94(9)$, $\text{H}\cdots\text{A} = 2.9(2)$, $\text{D}\cdots\text{A} = 3.337(12)$, $\angle\text{DHA} = 108(16)$; $\text{N}(1)-\text{H}(1)\cdots\text{O}(6)$ $\text{D}-\text{H} = 0.96(7)$, $\text{H}\cdots\text{A} = 2.80(9)$, $\text{D}\cdots\text{A} = 3.466(10)$, $\angle\text{DHA} = 128(8)$.

proximately 0.21 \AA out of the ring center toward the $\text{P}(3)-\text{P}(4)$ bond. The rubidium–phosphorus bond lengths are available in the caption of Figure 2. Each of the rubidium cations is coordinated by a molecule of 18-crown-6 with $\text{Rb}-\text{O}$ bond lengths in the range of $2.950(6)-3.225(6) \text{ \AA}$, and the rubidium ions are placed $1.207(2)$ and $1.214(3) \text{ \AA}$ away from the least-squares planes through the corresponding oxygen atoms. This yields a total coordination number of 10 for each rubidium cation and leads to a tripledecker-like complex, $(\text{Rb}@18\text{-crown-6})_2(\text{P}_4)_{0.85}(\text{As}_4)_{0.15}$ (Figure 2). To each molecule of 18-crown-6, a molecule of ammonia is attached via $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonding. The nitrogen atoms $\text{N}(1)$ and $\text{N}(2)$ are $2.302(9)$ and $2.155(8) \text{ \AA}$ above the least-squares planes defined by the oxygen atoms of the crown ether molecules. The $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond lengths and angles are available in the caption of Figure 2. The $\text{N}(3)$ nitrogen of a molecule of ammonia of crystallization is not coordinating. Figure 2 shows a projection of the unit cell along the a axis: the molecule of ammonia of crystallization is filling the voids between the molecular $(\text{Rb}@18\text{-crown-6}(\text{NH}_3)_2(\text{P}_4)_{0.85}(\text{As}_4)_{0.15})$ entities. Crystallographic details are found in Table 1.

The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of the liquid ammonia solution of the reaction mixture at $-40 \text{ }^\circ\text{C}$ shows two signals. The singlet at 336.0 ppm comes from the 6π aromatic P_4^{2-} anion. It is shifted to lower field compared to the signal in compound **1**, which is caused by the larger counteraction Rb^+ . This signal is also a singlet in the ^{31}P NMR spectrum. The signal at -268.9 ppm is a singlet in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum and a triplet with $^1J_{\text{P,H}} = 140 \text{ Hz}$ in the ^{31}P NMR spectrum; it comes from PH_2^- .

Structure of Bis(potassium(18-crown-6)cyclotetraarsenide ($\text{K}@18\text{-crown-6})_2\text{As}_4$ (3**)).** $(\text{K}@18\text{-crown-6})_2\text{As}_4$ was synthesized from potassium arsenide(5/4),³⁹ triphenylbismuth,

and 18-crown-6 in a liquid ammonia solution. The As_4^{2-} anion is the anionic moiety of this structure and is built up from two arsenic atoms on the common $4e$ positions of space group $P2_1/n$, located about 1.7 \AA away from a center of inversion (Wyckoff position $2a$), which generates the two other arsenic atoms. The $\text{As}-\text{As}$ bond lengths are $2.3871(4) \text{ \AA}$ for $\text{As}(1)-\text{As}(2)$ and $2.3898(4) \text{ \AA}$ for $\text{As}(1)-\text{As}(2)\#1$; the bond angles are $91.16(1)^\circ$ for $\text{As}(2)-\text{As}(1)-\text{As}(2)\#1$ and $88.84(1)^\circ$ for $\text{As}(1)-\text{As}(2)-\text{As}(1)\#1$. All other atoms also reside on the common $4e$ positions. The cyclotetraarsenide anion is coordinated by two symmetry equivalent potassium ions $\text{K}(1)$ and $\text{K}(1)\#1$ in an η^4 -like manner. The potassium ion resides $3.1571(7) \text{ \AA}$ above a least-squares plane defined by the arsenic atoms and is shifted slightly out of the center; the arsenic–potassium distances are in the range of about $3.5-3.7 \text{ \AA}$ and are found, together with some selected bond angles, in the caption of Figure 3. In addition, the potassium ion is coordinated by a molecule of 18-crown-6 yielding a coordination number of ten. The potassium ion is located $0.9040(9) \text{ \AA}$ above a least-squares plane through the oxygen atoms of the crown ether, and the $\text{K}-\text{O}$ distances are found in the caption of Figure 3. The center of inversion generates a $(\text{K}@18\text{-crown-6})_2\text{As}_4$ tripledecker-like complex which is shown on the left side of Figure 3. The packing of these molecules is shown in the projection of the unit cell on the bc plane on the right side of Figure 3. The crystallographic data are located in Table 1.

In Table 2 we show a comparison of the mean $\text{E}-\text{E}$ bond lengths ($\text{E} = \text{P}, \text{S}, \text{As}, \text{Se}$) for P_4^{2-} , P_6^{4-} , S_4^{2+} , As_4^{2-} , As_6^{4-} , and Se_4^{2+} obtained from single-crystal X-ray structures, which are not corrected for libration. The phosphorus–phosphorus bond length in the potassium species (**1**) is

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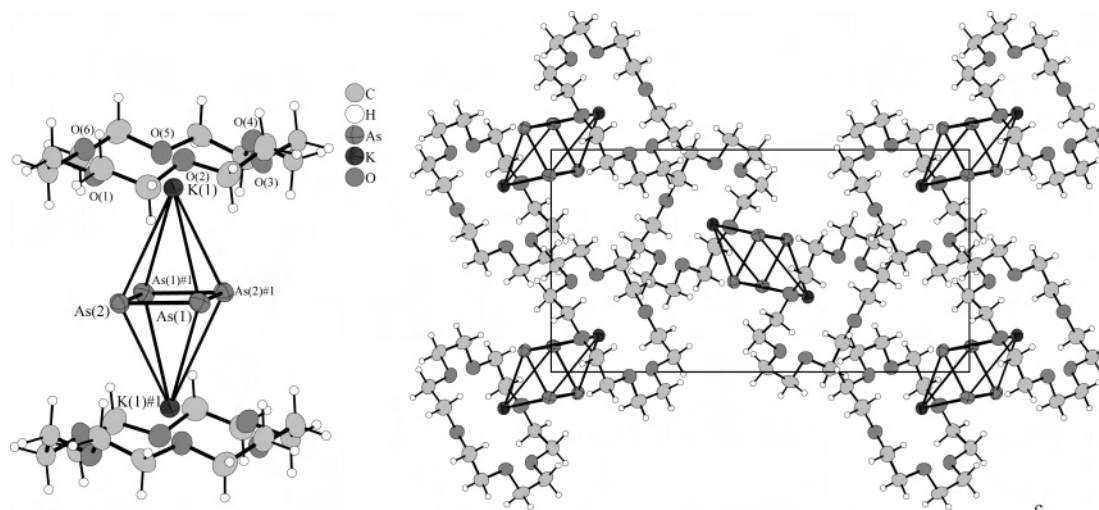


Figure 3. Projection of the $(\text{K}@18\text{-crown-6})_2\text{As}_4$ molecule (left) and a projection of the unit cell on the bc plane (right). Thermal ellipsoids are drawn at the 70% probability level. Selected bond lengths (\AA) and angles (deg): $\text{As}(1)\text{-K}(1) = 3.5697(6)$, $\text{As}(1)\text{-K}(1)\#1 = 3.5868(6)$, $\text{As}(2)\text{-K}(1) = 3.4958(6)$, $\text{As}(2)\text{-K}(1)\#1 = 3.6903(6)$, $\text{As}(2)\text{-As}(1)\text{-K}(1) = 73.561(13)$, $\text{As}(2)\#1\text{-As}(1)\text{-K}(1) = 68.572(14)$, $\text{As}(2)\text{-As}(1)\text{-K}(1)\#1 = 68.261(14)$, $\text{As}(2)\#1\text{-As}(1)\text{-K}(1)\#1 = 73.190(12)$, $\text{K}(1)\text{-As}(1)\text{-K}(1)\#1 = 124.298(11)$, $\text{As}(1)\text{-As}(2)\text{-K}(1)\#1 = 72.373(15)$, $\text{As}(1)\#1\text{-As}(2)\text{-K}(1)\#1 = 71.907(13)$, $\text{As}(1)\text{-As}(2)\text{-K}(1) = 68.092(13)$, $\text{As}(1)\#1\text{-As}(2)\text{-K}(1) = 68.500(13)$, $\text{K}(1)\#1\text{-As}(2)\text{-K}(1) = 123.388(12)$, $\text{K}(1)\text{-O}(1) = 2.844(2)$, $\text{K}(1)\text{-O}(3) = 2.878(2)$, $\text{K}(1)\text{-O}(5) = 2.905(2)$, $\text{K}(1)\text{-O}(6) = 2.925(2)$, $\text{K}(1)\text{-O}(2) = 3.014(2)$, $\text{K}(1)\text{-O}(4) = 3.094(2)$. Symmetry operations to generate equivalent atoms: $\#1\ 2-x, -y, -z$.

Table 2. Comparison of the Mean Bond Lengths in Homoatomic Cyclotetrapnictide Anions to the Cyclohexapnictide Anions and to the Isoelectronic Cyclotetrachalcogen Cations

compounds	mean $d(\text{E-E})$ ($\text{E} = \text{P, As}$) (\AA)	compounds	mean $d(\text{E-E})$ ($\text{E} = \text{S, Se}$) (\AA)
$(\text{K}@18\text{-crown-6})_2\text{P}_4 \cdot 8.5\text{NH}_3$ (1)	2.17	$\text{S}_4(\text{AsF}_6)_2(\text{AsF}_3)^{10}$	1.96
$(\text{Rb}@18\text{-crown-6})_2(\text{P}_4)_{0.85}(\text{As}_4)_{0.15} \cdot 3\text{NH}_3$ (2)	2.21		
$\text{Cs}_2\text{P}_4 \cdot 2\text{NH}_3$ ^{1,2}	2.15		
M_4P_6 ($\text{M} = \text{K, Rb, Cs}$) ($Fm\bar{3}m$) ²⁵⁻²⁸	2.16, 2.16, 2.14		
$[\text{Li}(\text{NH}_3)_4]_2\text{As}_4$ ³⁵	2.36	$\text{Se}_4(\text{Sb}_2\text{F}_4)(\text{Sb}_2\text{F}_5)(\text{SbF}_6)_5$ ⁴⁷	2.26
$[\text{Na}(\text{NH}_3)_5]_2\text{As}_4 \cdot 3\text{NH}_3$ ³⁵	2.35	$\text{Se}_4(\text{AlCl}_4)_2$ ⁴⁷	2.29
$(\text{K}@18\text{-crown-6})_2\text{As}_4$ (3)	2.39		
$[\text{Cs}_{0.35}\text{Rb}_{0.65}([2.2.2]\text{-crypt})]_2\text{As}_4 \cdot 2\text{NH}_3$ ³⁵	2.38		
M_4As_6 ($\text{M} = \text{Rb, Cs}$) ⁴⁸	2.38		

Table 3. Calculated Bond Lengths $d(\text{E-E})$ ($\text{E} = \text{P, S, As, Se}$) of P_4^{2-} , S_4^{2+} , As_4^{2-} , and Se_4^{2+} ^a

	HF		B3LYP		mean exptl bond length (\AA)
	6-311++G(3df) $d(\text{E-E})$ (\AA)	3-21G/6-311++G(3df) $d(\text{E-E})$ (\AA)	6-311++G(3df) $d(\text{E-E})$ (\AA)	3-21G/6-311++G(3df) $d(\text{E-E})$ (\AA)	
P_4^{2-}	2.1335	—	2.1670	—	—
K_2P_4	2.1402	2.1353	2.1774	2.1700	2.17
Rb_2P_4	—	2.1349	—	2.1690	2.21
Cs_2P_4	—	2.1322	—	2.1666	2.15
S_4^{2+}	1.9849	—	2.0412	—	1.96
As_4^{2-}	2.3616	—	2.4100	—	—
K_2As_4	2.3703	2.3668	2.4210	2.4158	2.39
Se_4^{2+}	2.2661	—	2.3301	—	2.26, 2.29

^a For As and Se, the 6-311G basis set was used. Following the crystal structures reported here, the structure of the M_2Pn_4 species ($\text{M} = \text{K, Rb, Cs}$; $\text{Pn} = \text{P, As}$) used in the calculations is of D_{4h} symmetry.

approximately 2.17 \AA which compares well to the P–P bond lengths in $\text{Cs}_2\text{P}_4 \cdot 2\text{NH}_3$ (about 2.15 \AA). However, the bond lengths in the rubidium compound (**2**) are significantly longer at 2.21 \AA , which is the result of the partial occupation of the site with As_4^{2-} . The bond shortening observed in going from P_4^{2-} to S_4^{2+} is easily understood and reproduced by the calculations, since there is less electron repulsion in the dication. The range of As–As bond lengths in the As_4^{2-} species encountered so far spans from about 2.35 to about 2.38 \AA and is confirmed by the calculations shown in Table 3. Naturally, the bond lengths in Se_4^{2+} are shorter than the ones in As_4^{2-} for the reason mentioned above. Overall, the calculated bond lengths are in good agreement with the

experimentally observed values. The bond lengths of the cyclotetrapnictides P_4^{2-} and As_4^{2-} are similar to the ones found in the M_4P_6 ($\text{M} = \text{K, Rb, Cs}$) and the M_4As_6 ($\text{M} = \text{Rb, Cs}$) species. They are also similar to the mean E–E distance ($\text{E} = \text{P, As}$) measured from the atoms in the trigonal basis to the formally negatively charged atoms in the heptaphosphanortricyclane anion, P_7^{3-} , and the heptaarsanortricyclane anion, As_7^{3-} , about 2.15 and 2.35 \AA , respectively.^{40–46} Since all of the bond lengths are the same, they

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Table 4. Basin Populations (Electrons) and Their Variances in the Polyarsenides As_4^{2-} , As_7^{3-} , and As_{11}^{3-} ^a

	As_4^{2-}	As_7^{3-}	As_{11}^{3-}
C(As) population and variance	27.75, 1.02	27.60, 1.07	27.59, 1.07
V(As–As) population and variance	2.07, 1.24	basal: 1.77, 1.13 basal to neg.: 2.02, 1.24 neg. to apical: 1.90, 1.18	As–As: 1.96, 1.18 As to neg.: 1.93, 1.19 As to apical: 1.98, 1.19
V(As) population and variance	3.65, 1.68	basal: 2.62, 1.32 form. neg.: 2.21, 1.17 apical: 2.43, 1.21	As: 2.42, 1.21 neg.: 2.24, 1.18 apical: 2.48, 1.25

^a C(As) are the core basins, V(As–As) the disynaptic valence basins (bonds), and V(As) the monosynaptic valence basins (lonepairs).

cannot be used as a criterion for the presence of aromatic bonds in these species; from the structural point of view, all the bonds are single bonds. Given the background of hydrocarbon aromatic compounds, this is unexpected, but an explanation is available from the examination of the bonding situation with the concept of ELF.

Within the theory of the electron localization function, we recently calculated the basin populations and variances of the phosphorus species P_7^{3-} , P_{11}^{3-} , P_4 , P_4^{2-} , and P_5^- and compared them to the central phosphorus–phosphorus single bond of the compound P_6H_8 .²⁴ The calculations have shown that the chemical bonds in P_7^{3-} and P_{11}^{3-} are very similar to each other and are also comparable to the central P–P bond in the reference compound, P_6H_8 . As was shown, they are essentially phosphorus–phosphorus single bonds. The P–P bond in P_4^{2-} and P_5^- also is a single bond compared to P_6H_8 , and neither the basin variances nor their covariance matrixes show the high variance of the disynaptic valence basins that would be expected for aromatic systems, as is the case for the aromatic hydrocarbons. However, high variances and large values in the covariance matrix are found for the lonepairs of P_4^{2-} and P_5^- , showing the delocalization of the electrons and indicating the aromaticity of these molecules.¹⁹ Compared to the classic aromatic hydrocarbons, we proposed to call this difference in behavior “lone pair aromaticity”.²⁴ In the next paragraph, we discuss the similarities and differences of As_7^{3-} , As_{11}^{3-} , and As_4^{2-} (Figure 4) to each other and the corresponding polyphosphides.

The first difference from the polyphosphides is encountered in the core basin populations and their variances. In P_4^{2-} , P_7^{3-} , and P_{11}^{3-} , the population of the phosphorus core basin is 10.06 electrons with a low variance of 0.43. This means that the neon shell of the phosphorus atoms is virtually intact. For arsenic, one would expect to find 28 electrons in the core basin (i.e., the noble gas configuration of argon plus 10 d electrons). However, the arsenic core basin populations in As_4^{2-} , As_7^{3-} , and As_{11}^{3-} show populations of just 27.6 electrons, approximately, with quite a high variance of about 1.05. This indicates that the d electrons participate in the

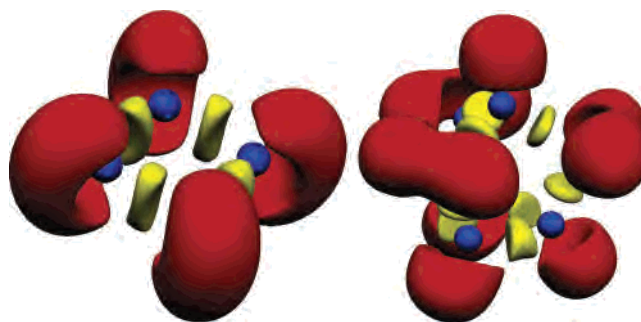


Figure 4. Electron localization function of As_4^{2-} ($\eta(r) = 0.72$) and As_7^{3-} ($\eta(r) = 0.72$). The core basins C(As) are color-coded in blue, the monosynaptic valence basins, V(As) (lonepairs), are in red, and the disynaptic valence basins, V(As–As) (bonds), are in yellow.

valence shell of arsenic (Table 4). The variances for mono- and disynaptic valence basins are therefore generally higher than in the phosphorus case. This finding is also substantiated by larger values in the covariance matrix compared to the values of the corresponding polyphosphides. The populations of the disynaptic valence basins of As_7^{3-} and P_7^{3-} are quite similar to each other. The disynaptic valence basin (i.e., the bond) population in the triangular base of P_7^{3-} is 1.71 electrons with a variance of 1.00, and because of d-orbital participation, in the congeneric As_7^{3-} , the population is increased to 1.77 electrons with a variance of 1.13. The same phenomenon (i.e., a higher population and variance in the arsenic species) is observed for the disynaptic valence basins between the atoms in the basal plane and the formally negatively charged ones (population/variance = 2.02/1.24 for As and 1.94/1.08 for P) and also for the disynaptic valence basins between the formally negatively charged and apical atoms (population/variance = 1.90/1.18 for As and 1.84/1.03 for P). The monosynaptic valence basins (lonepairs) also show this behavior, and the populations are higher than those of the disynaptic valence basins, as expected (basal plane atoms, monosynaptic valence population/variance = 2.62/1.32 for As and 2.30/1.00 for P; negatively formal charged atoms, population/variance = 2.21/1.17 for As and 1.98/0.96 for P; apical atoms, population/variance = 2.43/1.21 for As and 2.13/0.93 for P). The calculated values for As_{11}^{3-} are found in Table 4 and follow the same scheme.

Comparing As_4^{2-} and P_4^{2-} , one finds the disynaptic valence basins to be almost equally populated with 2.07 and 2.10 electrons, respectively, and for the reason given above, the variances are higher than the ones in P_4^{2-} (1.24 vs 1.12). Essentially, the As–As bond in As_4^{2-} can be called a single bond as can the P–P bond in P_4^{2-} . In both cases, the Pn–Pn single bond (Pn = P, As) only consists of one ELF

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maximum. The monosynaptic valence basins of As_4^{2-} show a high population with 3.65 electrons (3.31 electrons for P_4^{2-}) and a very high variance of 1.68 (1.31 for P_4^{2-}); there is only one ELF maximum on this level of theory. This drastically increased variance in the lonepairs is the major difference between As_4^{2-} and the other polyarsenides, As_7^{3-} and As_{11}^{3-} . The high variance indicates the site of electron delocalization and hence aromaticity.¹⁹ The covariance matrix supports this finding by showing a large cross-exchange contribution (0.13 electrons) between the monosynaptic valence basins of the arsenic atoms of As_4^{2-} , which is not encountered in the other polyarsenides considered (about 0.02 electrons). For the corresponding polyphosphides, the same behavior holds true.²⁴ Our calculations, along with the obvious homology to the corresponding phosphorus species,

lead us to the conclusion that the lonepairs of As_4^{2-} are the relevant electronic features for electron delocalization, and thus As_4^{2-} may be described as lone pair aromatic.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft DFG and the Fonds der Chemischen Industrie. F. Kraus thanks the Studienstiftung des Deutschen Volkes and the Fonds der Chemischen Industrie for a fellowship.

Supporting Information Available: Details of the preparation of the compounds, their structure solution, and refinement, more detailed NMR data, and the theoretical procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0514445