Synthesis and Spectroscopic and Structural Investigations of the 2,3,4,5-Tetraethylarsolides and -stibolides of the Alkali Metals Sodium, Potassium, Rubidium, and Cesium

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The reduction of 1-chloro-2,3,4,5-tetraethylarsole and -stibole with the alkali metals sodium, potassium, rubidium, and cesium in 1,2-dimethoxyethane (DME) or TMEDA yields the corresponding 2,3,4,5-tetraethylarsolides (L)M-AsC_4Et_4 [(L)M = (TMEDA)Na **1a**, $(DME)_{2/3}K$ **1b**, (DME)Rb **1c**, and (DME)Cs **1d**] and 2,3,4,5-tetraethylstibolides (L)M-SbC_4Et_4 [(L)M = $(DME)_{1/2}Na$ **2a**, (DME)Rb **2c**, and (DME)Cs **2d**]. These compounds are characterized by NMR spectroscopy and X-ray structure determinations. Whereas **1a** crystallizes with discrete dimeric molecules, all other compounds form one-dimensional polymers. With the exception of the sodium derivatives, all polymers show exclusively η^5-coordination of the arsolide and stibolide substituents. For the sodium compounds **1a** and **1b** also Na−As and Na−Sb σ-bonds, respectively, are observed.

Introduction

The phospholides are widely used reagents mainly for metathesis reactions in order to transfer the phospholide anion to a transition metal.[1] A systematic investigation of the alkali metal tetraethylphospholides showed that the sodium cation is too small to form a stack polymer with the metal center between two nearly coplanar aromatic ring systems.[2] Therefore, dimerization was observed and the metal atoms show a η^5-coordination to one phospholide substituent and a Na−P σ-bond to the other. Potassium 2,3,4,5-tetraethylphospholide forms a liner stack with strictly coplanar phospholide anions, whereas the larger alkali metal cations form zigzag stacks with additional Lewis bases such as 1,2-dimethoxyethane (DME) bonded to the metal atoms. For the alkali metal arsolides and stibolides far fewer investigations were published.

More than thirty years ago the first reports[3] on arsoles focused on the inversion barriers and aromaticity. The interest in this question remained for many years, and the aromaticity of the cyclopentadienides and the corresponding phospholides as well as the homologues were compared.[4,5] Twenty years thereafter a (TMEDA)lithium tetramethylarsolide was isolated and characterized by X-ray crystallography.[6] The molecular structure of this monomeric molecule resembled the characteristic features of the carbon analogues[7] such as η^5-coordination. Ring enlargement reactions of arsolides and the formation of arsabenzenes (arsinines) were reported by Märkl et al.[8]

The reaction of 2,3-dimethyl-1-phenylarsole with potassium yielded potassium 2,3-dimethylarsolide, which was used to prepare the corresponding 1-arsa- and 1,1′-diarsaferrocenes.[9] Furthermore, the application of potassium 2,5-bis(trimethylsilyl)-3,4-dimethylarsolide as an arsolide transfer reagent was also explored only a few years ago.[10,11] To our knowledge there are no reports on rubidium and cesium arsolides.

For more than twenty years the thermochromic purple-blue 2,2′,5,5′-tetramethyldistibolyl[12] and lithium stibolides[13,14] have been well-known. The application of the latter compound as a stibolide transfer reagent was explored by preparing the corresponding 1,1′-distibaferrocenes. An interesting synthesis of a PMDETA

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Table 1. NMR Data of the Alkali Metal 2,3,4,5-Tetraethylarsolides (1a–d) and -stibolides (2a–d) of the Type (L)M-EC$_4$Et$_4$ at 25 °C

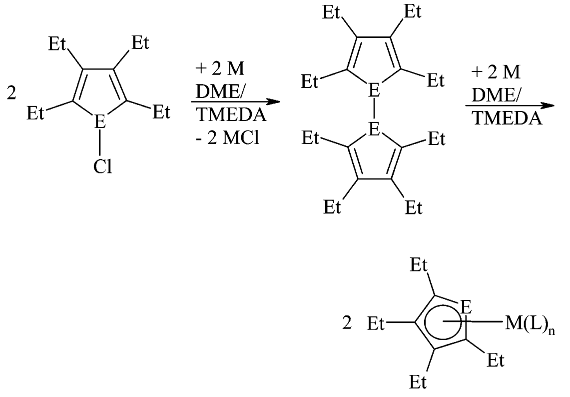
	Na	Na	K	K	Rb	Rb	Cs	Cs
E	As (**1a**)	Sb (**2a**)	As (**1b**)	Sb (**2b**)	As (**1c**)	Sb (**2c**)	As (**1d**)	Sb (**2d**)
L	TMEDA	1/2 DME	2/3 DME	1/3 THF	DME	DME	DME	DME
solvent	C_6D_6	C_6D_6	C_6D_6	C_6D_6	[D$_8$]THF	C_6D_6	[D$_8$]THF	[D$_8$]THF
^{1}H NMR								
$\delta(CH_3)$	1.15	1.07	0.95	1.01	1.22	1.03	1.00	1.03
$\delta(CH_2)$	2.60	2.50	2.39	2.22	2.66	2.49	2.37	2.42
^3J(H,H)	7.4	6.9	6.7	(broad)	7.7	7.5	7.6	7.5
$\delta(CH_3)$	1.48	1.39	1.24	1.01	1.47	1.37	1.19	1.24
$\delta(CH_2)$	2.97	2.85	2.70	2.43/2.83	2.90	2.84	2.63	2.70
^3J(H,H)	7.5	6.6	7.0	(broad)	7.4	7.2	7.4	7.1
$^{13}C\{^1H\}$ NMR								
$\delta(CH_3)$	17.3	16.5	16.7	15.2/16.1	16.4	16.0	16.3	15.9
$\delta(CH_3)$	20.3	21.0	19.4	18.9/21.2	19.0	20.8	18.7	20.4
$\delta(CH_2)$	22.0	23.8	21.7	23.1/23.7	21.6	23.7	21.6	23.7
$\delta(CH_2)$	26.0	29.2	25.6	26.5/29.1	25.5	29.0	25.3	28.7
δ(C3,C4)	132.4	138.8	131.4	150.2	131.1	138.2	132.1	138.4
δ(C2,C5)	156.3	161.8	156.9	153.3	156.8	164.6	158.1	166.2
lit.				16				

complex of 2-(3′,5′-dimethylphenyl)-5,7-dimethylstibindolyl potassium was reported by Breunig et al.[15] from trimesitylstibane and potassium in THF in the presence of the amine ligand. The crystals consisted of stacks of the (PMDETA)K$^+$ cations and stibindolyl anions. Semi(THF)potassium 2,3,4,5-tetraethylstibolide, which was prepared by reduction of octaethyldistibolyl, crystallized in a layer structure because the columns of alternating potassion and stibolide ions were interconnected by K–Sb σ-bonds.[16] To our knowledge there are no reports on the synthesis and molecular structures of stibolides of the heavier alkali metals rubidium and cesium, even though the properties of the phospholides of Rb and Cs differ from those of the smaller alkali metals.[17]

After our investigations regarding the 2,2′,3,3′,4,4′,5,5′-octaethyl-1,1′-diphosphaalkaline earth metallocenes[18] we were interested in the synthesis, physical properties, and molecular structures of the 2,3,4,5-tetraethylarsolides and -stibolides of the heavy alkali metals sodium, potassium, rubidium, and cesium. A comparison of the tetraethylphospholides, -arsolides, and -stibolides of the alkali metals allows the determination of the influence of pnictogen and metal atoms with different radii and electronegativities on the molecular structures and the NMR spectroscopic parameters.

Results and Discussion

Synthesis. The reduction of 2,3,4,5-tetraethyl-1-chloroarsole and -stibole with the heavier alkali metals sodium, potassium, rubidium, and cesium yields the corresponding alkali metal arsolides **1a–d** and stibolides **2a–d** (counterion Na (**a**), K (**b**), Rb (**c**), Cs (**d**)) according to eq 1. For crystallization purposes bidentate coligands such as 1,2-dimethoxyethane (DME) or 1,2-bis(dimethylamino)ethane (TMEDA) are convenient solvents for these reactions. If TMEDA is the solvent of the reaction, the excess of solvent was removed in vacuo and the product recrystallized from toluene.



(1)

E = As (**1**), Sb (**2**)
M = Na (**a**), K (**b**), Rb (**c**), Cs (**d**)

NMR Spectroscopy. The NMR parameters of the 2,3,4,5-tetraethylarsolides **1** and -stibolides **2** are summarized in Table 1; potassium 2,3,4,5-tetraethylstibolide is taken from the literature.[16] The influence of the alkali metals on the chemical shifts of the hydrogen and carbon atoms is far less pronounced than the variations caused by the pnictogen atoms. This fact is in agreement with the model of mainly ionic compounds, especially regarding the electronegativities according to Pauling: Whereas sodium has a value of 0.93, the heavier alkali metals show very similar electronegativities (K 0.82, Rb 0.82, and Cs 0.79).

The $^{13}C\{^1H\}$ NMR shifts of the 2,5-carbon atoms bound to the pnictogen atoms show expectedly the strongest variation toward lower field with increasing size of the pnictogen atom. The average values for the phospholides,[2] arsolides, and stibolides are $\delta = 145.5$, 157.0, and 164.2, respectively. The $^{13}C\{^1H\}$ NMR data of the ring carbon atoms of the well-known potassium 2,3,4,5-tetraethylstibolide (**2b**) form an exception from these trends; however, in all cases bidentate coligands are present, whereas for **2b** only THF was coordinated at the alkali metal.

In solution all 2,3,4,5-tetraethylstibolide anions are chemically and magnetically equivalent, whereas in the solid state this is only the case for the rubidium and cesium derivatives as well as for the dimeric TMEDA adduct of sodium 2,3,4,5-tetraethylarsolide (**1a**). Exchange and dissociation reactions lead to a magnetic

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Table 2. Radii of the Heavier Alkali Metal Cations (coordination number 6) and van der Waals Radii of the Pnictogen Atoms as Well as Bond Lengths of the Metal Atoms to the Pnictogen Atoms of the η^5-Bonded Ligands (Å)

	$r(M^+)$	P	As	Sb
$r(E)^a$		1.90	2.00	2.20
Na	1.16	2.939	3.030	3.160
K	1.52	3.204	3.327	3.507[16]
Rb	1.66	3.451	3.521	3.668
Cs	1.81	3.570	3.636	3.776

[a] van der Waals radii r of the pnictogen atoms E.

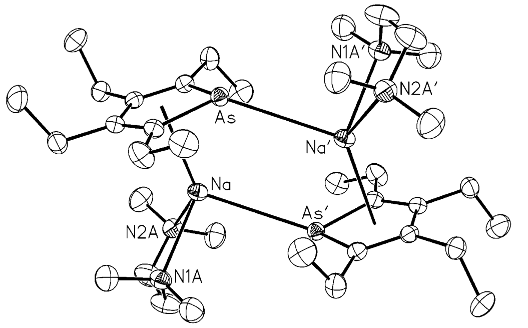

Figure 1. Molecular structure of dimeric (TMEDA)sodium 2,3,4,5-tetraethylarsolide (**1a**). The H atoms are omitted for reasons of clarity and the heavy atoms drawn at the 30% probability level. The prime symbols mark atoms generated by inversion symmetry. Selected bond lengths (Å): As−C1 1.888(3), As−C4 1.894(3), C1−C2 1.393(5), C2−C3 1.433(5), C3−C4 1.383(5), Na−As 3.030(1), Na−C1 2.989(4), Na−C2 3.002(4), Na−C3 2.912(4), Na−C4 2.851(4), Na−N1A 2.498(3), Na−N2A 2.583(3); angles (deg): C1−As−C4 86.5(2), N1A−Na−N2A 73.3(1), N1A−Na−As′ 94.06(9), N2A−Na−As′ 98.51(9), cent_{As}−Na−As′ 125.6.

equivalence on the NMR time scale, which can be expected for mainly ionic compounds.

Molecular Structures. The differences of molecular and crystal structures of the 2,3,4,5-tetraethylarsolides **1** and -stibolides **2** of the heavier alkali metals should be dominated by the differences of the radii of the metal atoms and of the pnictogen atoms. In Table 2 the radii of the relevant atoms are listed, and later on we will compare these data with the alkali metal−pnictogen distances to the η^5-bonded ligand of the observed structures.

Dimeric (TMEDA)sodium 2,3,4,5-tetraethylarsolide (**1a**) is represented in Figure 1. In the solid state discrete molecules are found with the sodium atoms bound in a η^5-manner to one arsolide anion and having a Na−As σ-bond to the other. Furthermore, the coordination sphere of the metal atom contains a bidentate TMEDA molecule.

Whereas **1a** resembles the molecular structure of the homologous phosphorus derivative, the heavier 2,3,4,5-tetraethylstibolide shows a totally different arrangement of the ions in the solid state. Due to the larger pnictogen atom, a chain structure is formed; however, similar structural motifs are found. Besides the η^5-coordination of the stibolide ligands also discrete Na−Sb bonds are observed. The chain structure of **2a** is given in Figure 2. This one-dimensional polymer can be cut into two characteristic moieties: a triple-decker anion and a disodium tetraethylstibolide cation. Within these fragments only η^5-coordination is observed; however, these moieties are connected by Na−Sb σ-bonds.

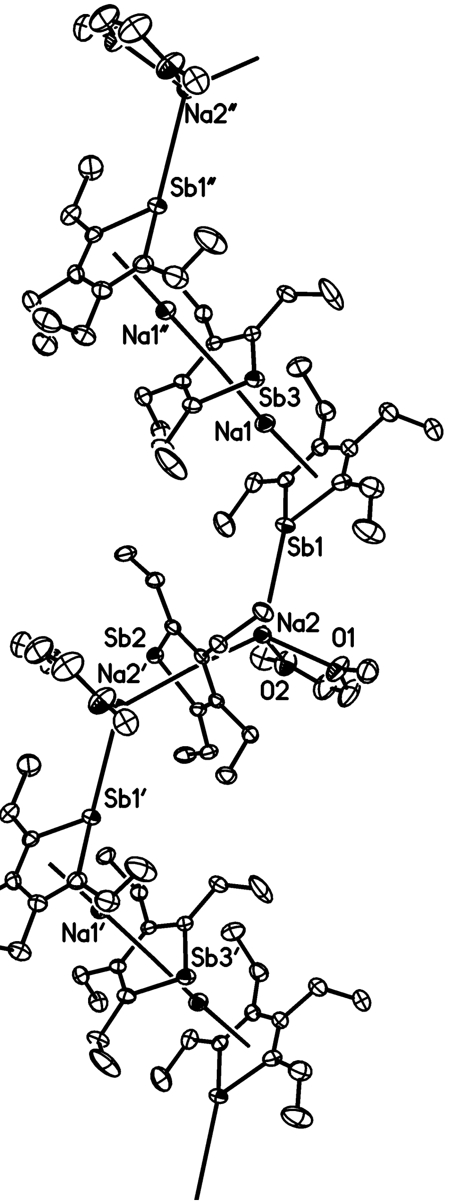

Figure 2. Molecular structure of polymeric semi(DME)-sodium 2,3,4,5-tetraethylstibolide (**2a**). The hydrogen atoms are not shown, and the ellipsoids represent a probability of 30%. The symmetry-related atoms are marked with a prime and generated by transposition parallel to the c axis (x, y, $z\pm1$). Selected bond lengths (Å): Sb1−C1 2.105(4), Sb1−C4 2.109(4), C1−C2 1.379(5), C2−C3 1.441(6), C3−C4 1.370(6), Sb2−C14 2.121(4), C13−C14 1.378(5), C13−C13′ 1.472(7), Sb3−C20 2.116(4), C19−C20 1.384(5), C19−C19′ 1.462(7), Na1−Sb1 3.049(2), Sb1−Na2 3.233(2), Sb2−Na2 3.196(2), Sb3−Na1 3.124(2).

In contrast to the potassium 2,3,4,5-tetraethylphospholide,[2] which crystallizes as a linear stack of alternating cations and η^5-bonded anions, the homologous arsolide **1b** forms a zigzag chain as shown in Figure 3. This one-dimensional polymer can be separated in a sandwich-like anion $[(\eta^5\text{-AsC}_4\text{Et}_4)\text{-K-}(\eta^5\text{-AsC}_4\text{Et}_4)]^-$ and a cation of the structure $[(\text{DME})\text{K-}(\mu,\eta^5\text{-AsC}_4\text{Et}_4)\text{-K(DME)}]^+$. However, only η^5-coordination of the 2,3,4,5-tetraethylarsolide is observed. The bending of the chain occurs at the DME bearing potassium cations. The

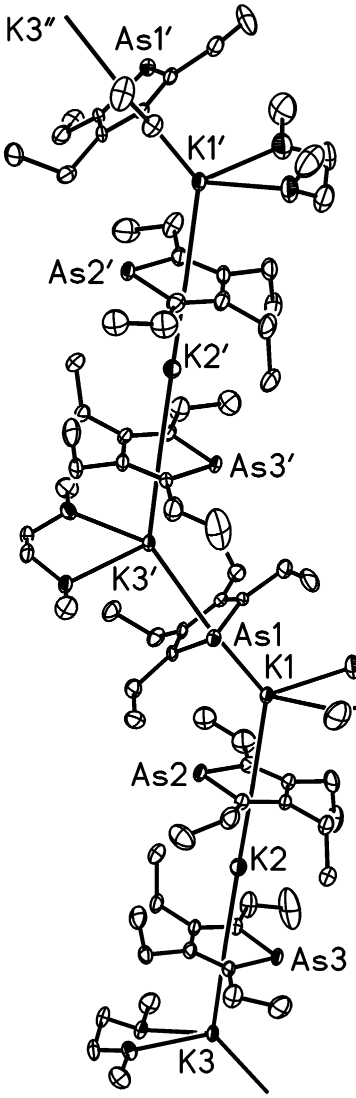

Figure 3. Molecular structure of (DME)$_{2/3}$K(AsC$_4$Et$_4$) (**1b**). The hydrogen atoms are not shown for clarity reasons, and the heavy atoms are drawn at the 30% probability level. The atoms marked with a prime are generated by transposition along the *c* axis. Selected bond lengths (Å): As1−C1 1.899(5), As1−C4 1.893(5), C1−C2 1.370(7), C2−C3 1.445(8), C3−C4 1.375(7), As2−C13 1.897(6), As2−C16 1.880(6), C13−C14 1.393(8), C14−C15 1.419(9), C15−C16 1.377(9), As3−C25 1.898(5), As3−C28 1.889(5), C25−C26 1.382(7), C26−C27 1.431(7), C27−C28 1.388(7), K1−As1 3.390(2), K1−As2 3.325(1), K2−As2 3.288(1), K2−As3 3.279(1), K3−As3 3.354(1), K1−O1 2.793(5), K1−O2 2.719(5), K3−O3 2.827(4), K3−O4 2.703(4).

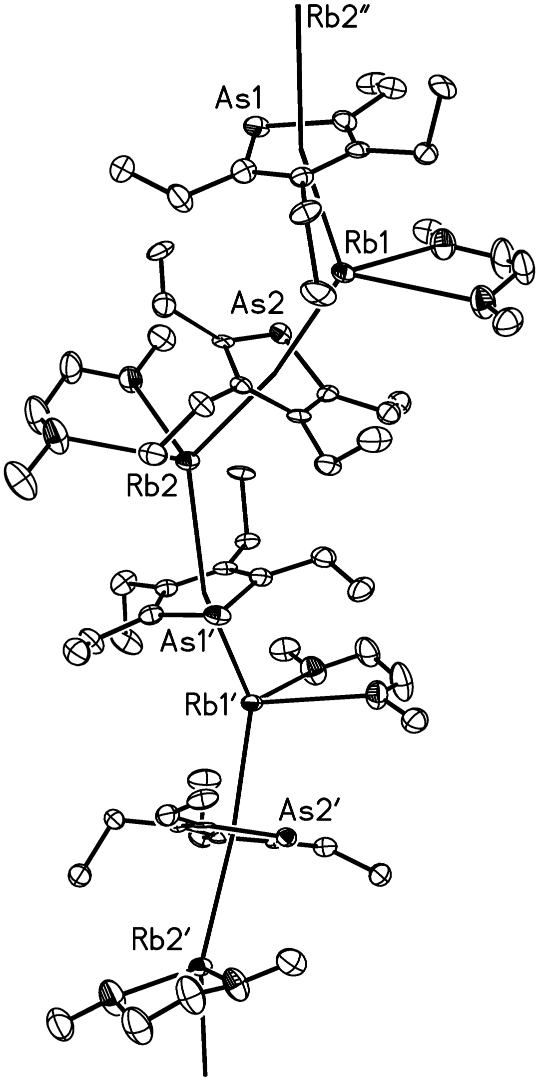

Figure 4. Molecular structure of (DME)rubidium 2,3,4,5-tetraethylarsolide (**1c**). The H atoms are omitted for clarity reasons, and the heavy atoms are shown at the 30% probability level. Symmetry-related atoms are marked either with one (x+0.5, −y+0.5, z−0.5) or with two primes (x−0.5, −y+0.5, z+0.5). [The homologous stibolide crystallizes isotypically, and therefore, the values of **2c** are given in parentheses.] Selected bond lengths (Å): As1−C1 1.907(7) [Sb1−C1 2.100(6)], As1−C4 1.897(7) [Sb1−C4 2.109(6)], C1−C2 1.397(9) [1.397(8)], C2−C3 1.429(10) [1.473(8)], C3−C4 1.392(9) [1.388(8)], As2−C13 1.902(6) [Sb2−C13 2.089(6)], As2−C16 1.908(7) [Sb2−C16 2.102(6)], C13−C14 1.407(9) [1.380(9)], C14−C15 1.433(9) [1.451(9)], C15−C16 1.394(9) [1.387(8)], Rb1−As1 3.582(1), Rb1−As2 3.4367(9), Rb1−O1 2.922(6) [2.943(5)], Rb1−O2 3.082(6) [3.033(5)], Rb2−As2 3.523(1), Rb2−As1′ 3.542(1), Rb2−O3 2.996(6) [2.965(5)], Rb2−O4 2.982(5) [2.996(5)], [Rb1−Sb1 3.5822(7), Rb1−Sb2 3.7272(7), Rb2−Sb2 3.6977(7), Rb2−Sb1′ 3.6646(8)]; angles (deg): Rb2″−cent$_{\mathrm{As1}}$−Rb1 163.4, cent$_{\mathrm{As1}}$−Rb1−cent$_{\mathrm{As2}}$ 133.6, Rb1−cent$_{\mathrm{As2}}$−Rb2 170.6, cent$_{\mathrm{As2}}$−Rb2−cent$_{\mathrm{As1'}}$ 130.3 [Rb2″−cent$_{\mathrm{Sb1}}$−Rb1 172.4, cent$_{\mathrm{Sb1}}$−Rb1−cent$_{\mathrm{Sb2}}$ 130.2, Rb1−cent$_{\mathrm{Sb2}}$−Rb2 163.0, cent$_{\mathrm{Sb2}}$−Rb2−cent$_{\mathrm{Sb1'}}$ 130.3].

structure of potassium 2,3,4,5-tetraethylstibolide (**2b**) was reported earlier.[16]

The 2,3,4,5-tetraethylarsolides of rubidium (**1c**) and cesium (**1d**) as well as the homologous 2,3,4,5-tetraethylstibolides **2c** and **2d** crystallize as zigzag chains with the bending at the alkali metal atoms, which are also bonded to DME molecules. These structures are very similar to those of the corresponding 2,3,4,5-tetraethylphospholides.[2] The molecular structure of rubidium 2,3,4,5-tetraethylarsolide **2b** is represented in Figure 4, and the homologous cesium compounds **1d** and **2d** are shown in Figures 5 and 6, respectively. Rubidium 2,3,4,5-tetraethylstibolide **2c** crystallizes isotypically to the stibolide **2b**, and therefore, the representation of its molecular structure is redundant. However, selected bond lengths of **2c** are given in parentheses in Figure 4.

In Table 2 characteristic bond lengths are summarized. The molecular structures of the 2,3,4,5-tetra-

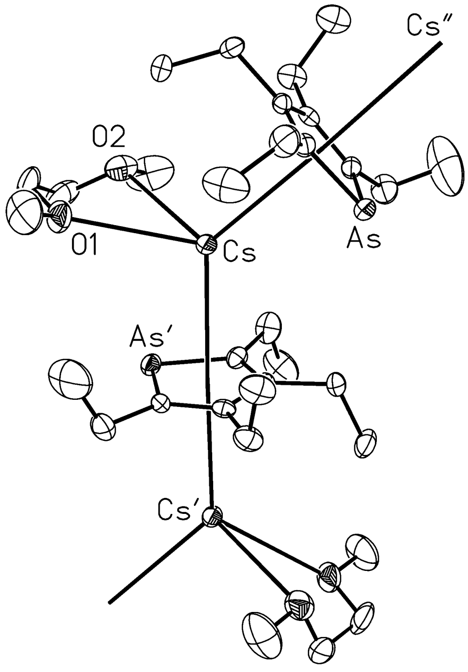

Figure 5. Molecular structure of polymeric (DME)cesium 2,3,4,5-tetraethylarsolide (**1d**). The H atoms are omitted for clarity reasons, and the C atoms are shown at the 30% probability level. Symmetry-related atoms are marked with one ($-x$+0.5, y+0.5, $-z$+0.5) or two primes ($-x$+0.5, y−0.5, $-z$+0.5). Selected bond lengths (Å): As−C1 1.895(6), As−C4 1.870(7), C1−C2 1.369(9), C2−C3 1.439(8), C3−C4 1.389(8), Cs−As 3.6264(8), Cs−As′ 3.6462(8), Cs−O1 3.119(5), Cs−O2 3.132(5); angles (deg): $\text{cent}_{\text{As}'}$−Cs−cent_{As} 132.4, Cs−cent_{As}−Cs′ 177.2.

ethylarsolides and -stibolides of rubidium and cesium are alike. The difference of the radii of the cations Rb^+ and Cs^+ is larger ($\Delta r(\text{Cs}^+-\text{Rb}^+) = 15$ pm) than the $\text{M}-\text{E}^{\text{V}}$ bond length differences of the corresponding phospholides ($\Delta r = 11.9$ pm), arsolides ($\Delta r = 11.5$ pm), and stibolides ($\Delta r = 10.8$ pm). This fact is a consequence of the softness and hence deformation of the large alkali metal cations. A comparison of the $\text{K}-\text{E}^{\text{V}}$ bond lengths of the phospholide, arsolide **1b**, and stibolide **2b** shows that the phospholide shows unexpected small K−P distances. The potassium 2,3,4,5-tetraethylphospholide[2] crystallizes in a linear chain structure, whereas the larger pnictogen atoms enforce an opening of the structure and DME ligands are bound to two of three potassium atoms. This enlargement of the coordination sphere of the metal atoms leads to a larger increase of the K−As bond lengths than expected. Similar considerations are true going from the potassium complexes to the rubidium derivatives where DME ligands are coordinated to all Rb^+ atoms.

Dependent on the size of the alkali metal atom we find no DME coligands (K-PC_4Et_4[2]), a coordination to only a part of the metal atoms (**1b** and **2b**[16]), or a coordinative saturation of all metal centers by ether coligands (**1c**, **1d**, **2c**, and **2d**). The size of the metal and pnictogen atoms determines the degree of bending of the one-dimensional polymers. They can reduce steric strain not only by expanding the $\text{M}-\text{E}^{\text{V}}$ bond lengths but also by an enlargement of the angles at the metal centers as well as the M−cent_{E}−M values [cent_{E} = center of the arsolide (E = As) or stibolide substituent (E = Sb) calculated from the ring pnictogen and carbon atoms]. For example, in **1c** corresponding Rb1−cent_{As1}−Rb2″ and Rb1−cent_{As2}−Rb2 values of 163.4° and 170.6° are observed, whereas in **1d** a larger angle Cs−cent_{As}−Cs″ of 177.2° is found.

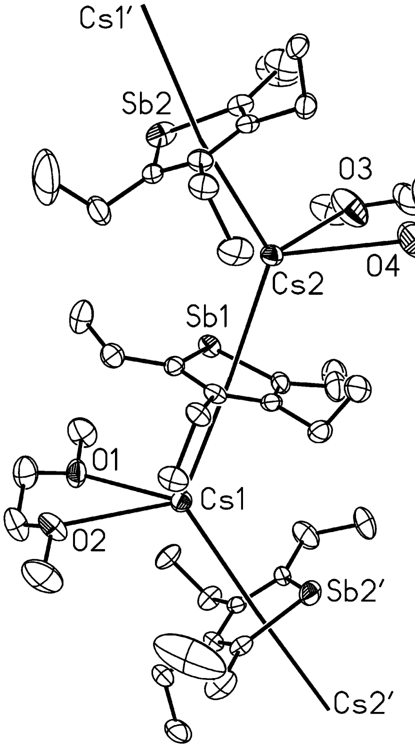

Figure 6. Molecular structure of polymeric (DME)cesium 2,3,4,5-tetraethylstibolide (**2d**). The hydrogen atoms are not drawn for clarity reasons, and the heavy atoms are shown with a probability of 30%. Cs1′ is generated by the symmetry operation (x+0.5, $-y$+1.5, z−0.5); the other atoms marked with a prime are generated by the symmetry operation (x−0.5, $-y$+1.5, z+0.5). Selected bond lengths (Å): Sb1−C1 2.091(8), Sb1−C4 2.110(8), C1−C2 1.40(1), C2−C3 1.43(1), C3−C4 1.40(1), Sb2−C17 2.064(8), Sb2−C20 2.101(9), C17−C18 1.38(1), C18−C19 1.43(1), C19−C20 1.37(1), Cs1−Sb2′ 3.7756(9), Cs2−Sb1 3.7752(9), Cs2−Sb2 3.778(1), Cs1−O1 3.105(6), Cs1−O2 3.214(7), Cs2−O3 3.047(6), Cs2−O4 3.28(1); angles (deg): Cs1′−cent_{Sb2}−Cs2 171.9, cent_{Sb2}−Cs2−cent_{Sb1} 133.0, Cs2−cent_{Sb1}−Cs1 172.3, cent_{Sb1}−Cs1−$\text{cent}_{\text{Sb2}'}$ 126.0.

The bidentate DME coligand prevents an interconnection of these one-dimensional polymers. Furthermore, short alkali metal−ethyl contacts (for a detailed review on agostic interactions of d^0-metal complexes see the literature[19]) also enhance the steric and electronic saturation of the metal cations. In the case of coordinated monodentate THF molecules as additional Lewis bases a linkage of the one-dimensional polymers was observed in the THF complex of potassium 2,3,4,5-tetraethylstibolide.[16]

Another question addressed to these compounds concerns the aromaticity of the arsolides and stibolides. The extent of delocalization of the anionic charge can be estimated by comparison of the endocyclic C−C bond lengths of the 2,3,4,5-tetraethylphospholides,[2] -arsolides, and -stibolides (Table 3). A lower degree of

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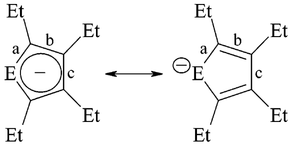
Table 3. Comparison of the Endocyclic Bond Lengths (Å) of the 2,3,4,5-Tetraethylphospholides, -arsolides, and -stibolides of the Heavy Alkali Metals[a]



E		P	As	Sb
Na	*a*	1.76	1.891	2.113
	b	1.40	1.388	1.378
	c	1.43	1.433	1.458
	$\Delta\,(c - b)$	0.03	0.045	0.080
K	*a*	1.760	1.893	2.097
	b	1.401	1.381	1.39
	c	1.427	1.432	1.45
	$\Delta\,(c - b)$	0.026	0.051	0.06
Rb	*a*	1.770	1.904	2.100
	b	1.395	1.398	1.395
	c	1.434	1.431	1.462
	$\Delta\,(c - b)$	0.039	0.033	0.067
Cs	*a*	1.767	1.883	2.092
	b	1.398	1.379	1.39
	c	1.416	1.439	1.43
	$\Delta\,(c - b)$	0.018	0.060	0.04

[a] The differences Δ (Å) between the bond lengths *b* and *c* show the degree of delocalization of the anionic charge.

delocalization leads to a larger difference Δ ($\Delta = c - b$) between the bond lengths *b* and *c*, but also to a larger anionic charge on the pnictogen atom E, and consequently, the E−C distances are closer to a characteristic single bond than to a double bond. Whereas for the phospholides the aromaticity was already supported by theoretical considerations,[4,5] the difference Δ increases with the size of the pnictogen atom. This is a consequence of an increasing size of the p-orbitals at E and results in a loss of overlap with the carbon-centered π-system. Therefore the Sb−C bonds (average Sb−C bond length for **2a** to **2d**: 2.10 Å) are clearly longer than observed for a $Sb{=}C$ double bond (2.06 Å),[20] calculated for stibaethene $H{-}Sb{=}CH_2$ (2.01 Å)[21] or found for stibabenzene (stibinine, 2.05 Å).[22] On the other hand, similar discrepancies are also valid even for the phospholides (average P−C bond length for the phospholides: 1.764 Å, Table 3); in comparison to phosphaethene (1.673 Å)[23] and to phosphabenzene (phosphinine, 1.73 Å)[24] larger P−C distances are found for the alkali metal 2,3,4,5-tetraethylphospholides. Therefore, the difference $\Delta = c - b$ seems to be a more reliable value to estimate the degree of delocalization of the anionic charge and the loss of aromaticity within these 6π-electron systems. In general the discrepancy Δ increases with the size of the pnictogen atom, which can be interpreted in the sense of decreasing charge delocalization and consequently decreasing aromatic character of the 6π-electron system of the cycle. This finding is in agreement with the expectation because the overlap of the pnictogen-centered p-orbital (which increases from P to Sb) with the carbon-centered π-system should decrease due to increasing E−C bond lengths and an increasing misfit of the size of the p_E- and p_C-orbitals.

Summary

A straightforward high-yield synthesis allows the preparation of the alkali metal 2,3,4,5-tetraethylarsolides and -stibolides. These mainly ionic compounds form one-dimensional polymers in the solid state with the exception of the sodium derivatives. The arsolide **1a** forms a dimer, whereas in the stibolide **2a** Na−Sb σ-bonds are observed besides the η^5-coordination. The molecular structures and the amount of DME coligands are dependent on the size of the alkali metals. In **2a** only half of the sodium atoms are bound to a DME coligand; in **1b** two-thirds of the potassium cations are coordinated to DME molecules, whereas in all rubidium and cesium arsolides and stibolides every metal center is carrying an ether coligand.

Experimental Part

All experiments and manipulations were carried out under an atmosphere of argon. Reactions were performed by using standard Schlenk techniques and in dried and thoroughly deoxygenated solvents. The NMR data were obtained at room temperature and are summarized in Table 1. For the IR spectra the crystalline compounds were dissolved in Nujol and measured between KBr windows. The starting 1-chloro-2,3,4,5-tetraethylarsole and -stibole were prepared according to a literature procedure.[18] All alkali metal 2,3,4,5-tetraethylarsolides and -stibolides are extremely sensitive toward moisture and air.

(TMEDA)sodium 2,3,4,5-tetraethylarsolide (1a). 1-Chloro-2,3,4,5-tetraethylarsole (4.87 g, 17.7 mmol) was dissolved in 30 mL of TMEDA, and an excess of sodium was added to this solution at room temperature. Within 3 days the solution turned dark brown. Then the solvent was removed at reduced pressure and the residue redissolved in 50 mL of toluene. After removal of all solid materials (NaCl) the volume was reduced and at −20 °C 4.55 g of light brown crystals of **1a** (12.0 mmol, 68%) was obtained. Mp: 250 °C. Anal. Calcd for $C_{18}H_{36}N_2AsNa$, 378.40: C 57.13, H 9.59. Found: C 57.13, H 8.81. IR: 1605 w, 1585 m, 1526 w, 1495 w, 1475 s, 1436 s, 1415 m, 1382 m, 1371 m, 1310 m, 1293 m, 1251 m, 1177 w, 1155 m, 1133 m, 1112 w, 1097 w, 1079 m, 1050 m, 1033 s, 995 m, 951 w, 928 w, 870 w, 827 w, 785 w, 778 w, 747 w, 728 m, 695 vw, 656 vw, 638 vw, 621 vw, 583 vw, 543 vw, 488 vw, 464 vw, 426 vw, 405 vw, 347 vw, 321 vw, 305 vw.

General Procedure for Potassium, Rubidium, and Cesium 2,3,4,5-Tetraethylarsolide (**1b**, **1c**, and **1d**, respectively). 1-Chloro-2,3,4,5-tetraethylarsole was dissolved in 50 mL of DME and an excess (potassium) or a stoichiometric amount of alkali metal added. After a reaction period of several days the volume of the dark brown solution was reduced to a few milliliters, and at −20 °C crystalline alkali metal arsolides were obtained. The reaction conditions and the yields are given in Table 4.

1b: Anal. Calcd for $C_{16}H_{30}O_2AsK$, 368.42: C 52.16, H 8.21. Found: C 54.97, H 8.09. IR: 1455 s, 1403 vw, 1374 m, 1311 w, 1250 vw, 1193 vw, 1133 vw, 1086 w, 1050 w, 1021 w, 1006 w, 965 vw, 930 vw, 870 vw, 853 vw, 824 w, 780 w, 726 vw, 542 vw.

1c: Anal. Calcd for $C_{16}H_{30}O_2AsRb$, 414.79: C 46.33, H 7.29. Found: C 48.37, H 7.39. IR: 1648 vw, 1574 w, 1529 w, 1471 m, 1450 s, 1408 w, 1369 m, 1311 m, 1287 vw, 1245 w, 1207

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Table 4. Reaction Conditions for the Synthesis of the DME Complexes of M-AsC_4Et_4 as Well as the Yields of 1b, 1c, and 1d

M	amount of M	amount of $ClAsC_4Et_4$	reaction time (days)	product	color	yield (g, mmol, %)	mp (°C)
K	excess	4.1 g, 14.9 mmol	5	**1b**	brown	4.20, 11.4, 77	157
Rb	2.0 g, 23.4 mmol	3.2 g, 11.7 mmol	4	**1c**	brown	3.68, 8.87, 76	210
Cs	1.0 g, 7.52 mmol	1.0 g, 3.76 mmol	4	**1d**	brown	1.64, 3.54, 94	173

Table 5. Reaction Conditions for the Synthesis of the DME Complexes of M-SbC_4Et_4 as Well as the Yields of 2a, 2c, and 2d

M	amount of M	amount of $ClSbC_4Et_4$	reaction time (days)	product	color	yield (g, mmol, %)	mp (°C)
Na	excess	2.2 g, 6.88 mmol	5	**2a**	yellow	2.56, 6.40, 93	174 (dec)
Rb	2.0 g, 23.4 mmol	3.8 g, 11.7 mmol	2	**2c**	gray	3.69, 9.90, 85	>300
Cs	1.0 g, 7.52 mmol	1.2 g, 3.76 mmol	2	**2d**	green	1.67, 3.27, 87	250

Table 6. Crystallographic Data and Details of the Refinement Procedures for the 2,3,4,5-Tetraethylarsolides 1 (E^V = As) and -stibolides 2 (E^V = Sb) of the Alkali Metals M = Na (a), K (b), Rb (c), and Cs (d)

compd (M/E^V)	**1a** (Na/As)	**1b** (K/As)	**1c** (Rb/As)	**1d** (Cs/As)	**2a** (Na/Sb)	**2c** (Rb/Sb)	**2d** (Cs/Sb)
empirical formula	$C_{43}H_{80}As_2N_4Na_2$	$C_{44}H_{80}As_3K_3O_4$	$C_{32}H_{60}As_2O_4Rb_2$	$C_{16}H_{30}AsCsO_2$	$C_{28}H_{50}Na_2O_2Sb_2$	$C_{32}H_{60}O_4Rb_2Sb_2$	$C_{32}H_{60}Cs_2O_4Sb_2$
fw ($g \cdot mol^{-1}$)	848.945	1015.16	829.58	462.23	708.16	923.24	1018.12
temp T (K)	200(2)	200(2)	193(2)	193(2)	193(2)	193(2)	193(2)
space group[26]	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	Cc (no. 9)
a (Å)	9.2615(2)	9.8350(9)	13.863(2)	10.8517(8)	26.088(1)	14.017(1)	14.510(3)
b (Å)	16.6347(3)	16.654(1)	17.033(3)	11.807(1)	16.253(1)	17.082(2)	17.010(3)
c (Å)	16.1150(3)	32.621(4)	16.497(2)	15.751(1)	17.3349(7)	16.681(2)	16.840(3)
α (deg)	90	90	90	90	90	90	90
β (deg)	104.5701(8)	102.77(1)	91.581(3)	96.962(9)	117.021(1)	91.246(2)	92.542(4)
γ (deg)	90	90	90	90	90	90	90
V ($Å^3$)	2402.87(8)	5211.1(9)	3893.8(10)	2003.2(3)	6547.5(5)	3993.0(7)	4152.2(12)
Z	2	4	4	4	8	4	4
ρ_{calcd} ($g \cdot cm^3$)	1.173	1.294	1.415	1.533	1.437	1.536	1.629
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	1.440	2.187	4.230	3.488	1.697	3.804	3.057
no. of indep reflns	4203	7601	6408	3807	4350	5654	5346
obs reflns ($I > 2\sigma(I)$)	3357	4573	4610	1964	3364	4693	4646
abs corr	numerical	none	SADABS	SADABS	none	SADABS	none
min./max. transmn	0.713/0.912		0.185/1.000	0.631/0.827		0.592/1.000	
$wR_2{}^a$ (on F^2, all data)	0.1369	0.1119	0.1941	0.0739	0.0668	0.1282	0.0678
$R_1{}^a$ ($I > 2\sigma(I)$)	0.0482	0.0467	0.0679	0.0368	0.0279	0.0439	0.0296
goodness-of-fit S^b on F^2	1.052	0.890	1.001	0.772	0.926	1.061	0.949

[a] Definition of the R indices: $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o{}^2) + (aP)^2$. [b] $S = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/(N_o - N_p)\}^{1/2}$.

vw, 1194 w, 1155 vw, 1131 m, 1090 m, 1050 m, 1023 m, 1006 m, 969 m, 936 vw, 912 vw, 857 s, 848 m, 826 m, 804 w, 772 w, 718 m, 705 w, 676 vw, 635 vw, 570 vw, 546 vw, 529 vw, 480 vw, 476 vw, 459 vw, 394 w, 364 w, 345 vw, 293 vw.

1d: Anal. Calcd for $C_{16}H_{30}O_2AsCs$, 462.22: C 41.57, H 6.54. Found: C 41.57, H 6.37. IR: 1598 vw, 1456 m, 1409 w, 1374 w, 1364 w, 1310 w, 1247 w, 1136 vw, 1048 m, 1017 m, 930 vw, 860 w, 840 w, 826 w, 798 w, 780 w, 768 w, 722 vw, 670 vw, 657 vw, 635 vw, 541 vw, 532 vw, 472 vw, 446 vw.

General Procedure for Sodium, Rubidium, and Cesium 2,3,4,5-Tetraethylstibolide (**2a**, **2c**, and **2d**, respectively). 1-Chloro-2,3,4,5-tetraethylstibole was dissolved in 50 mL of DME as given in Table 5. The alkali metals were added to this solution, which was stirred at room temperature for several days. During this time the color of the solution turned dark brown or in the case of the preparation of the cesium derivative greenish brown. After the reaction time given in Table 5 all solid materials were removed and then the volume of the solution was reduced to a few milliliters. Crystalline materials precipitated during the storage at −20 °C.

2a: Anal. Calcd for $C_{16}H_{30}O_2NaSb$, 399.19: C 48.14, H 7.58. Found: C 48.18, H 7.56. IR: 1640 vw, 1582 vw, 1454 vs, 1411 w, 1396 vw, 1371 m, 1308 w, 1253 m, 1190 vw, 1120 w, 1084 s, 1061 s, 1047 s, 1010 s, 925 vw, 860 m, 798 s, 771 m, 702 vw, 660 vw, 531 vw.

2c: Anal. Calcd for $C_{16}H_{30}O_2RbSb$, 461.67: 41.62, H 6.55. Found: C 41.60, H 6.53. IR: 1455 s, 1406 w, 1367 m, 1308 w, 1287 vw, 1244 w, 1208 vw, 1195 vw, 1156 vw, 1130 m, 1117 w, 1089 vs, 1046 w, 1032 m, 1023 m, 966 vw, 925 vw, 857 m, 848 w, 800 vw, 780 vw, 766 vw, 722 vw, 669 vw, 655 vw, 629 vw, 607 vw, 568 vw, 510 vw, 434 vw, 384 vw, 343 vw.

2d: Anal. Calcd for $C_{16}H_{30}O_2CsSb$, 509.10: C 37.75, H 5.94. Found: C 37.75, H 6.14. IR: 1455 s, 1407 m, 1366 m, 1342 vw, 1307 m, 1287 vw, 1246 m, 1193 vw, 1115 s, 1093 s, 1079 m, 1045 m, 1005 vs, 980 s, 926 vw, 854 m, 848 m, 799 m, 782 m, 737 vw, 723 m, 712 vw, 675 vw, 638 vw, 607 vw, 569 vw, 539 vw, 451 vw, 392 w, 375 vw.

X-ray Structure Determinations. Data were collected on a Siemens P4 diffractometer with a Siemens SMART-CCD area detector (**1c**, **2a**, **2c**, **2d**) or on a STOE IPDS diffractometer (**1a**, **1b**, **1d**) with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using oil-coated rapidly cooled single crystals.[25] Crystallographic parameters, details of data collection, and refinement procedures are summarized in Table 6.

The structures were solved by direct methods with the program SIR97[27] and refined with the software packages SHELXL-93 and SHELXL-97.[28] Neutral scattering factors

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were taken from Cromer and Mann[29] and for the hydrogen atoms from Stewart et al.[30] The non-hydrogen atoms were considered with a riding model under restriction of ideal tetrahedral symmetry at the corresponding carbon atoms.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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