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Niobium–Arsenic Zintl Phases: A_6NbAs_5 (A = K, Rb, Cs), $K_6NbTlAs_4$, and $K_8NbPbAs_5$ with Edge-Bridged Niobium-Centered Tetrahedra of Arsenic, $[NbAs_4M]^{n-}$ Where M = As, Tl, Pb

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The five title compounds were prepared by direct reactions of the corresponding elements at high temperature. Their structures contain isolated anions of tetrahedral $NbAs_4$ where one of the edges of the tetrahedron is bridged by a third atom. The bridging atom is arsenic in A_6NbAs_5 (monoclinic, $P2_1/c$, $Z = 8$; with $a = 25.774(3)$ Å, $b = 9.335(1)$ Å, $c = 13.012(1)$ Å, $\beta = 101.05(1)°$ for A = K; $a = 27.629(1)$ Å, $b = 9.925(1)$ Å, $c = 14.111(1)$ Å, $\beta = 101.63(1)°$ for A = Rb; and $a = 27.405(1)$ Å, $b = 9.9447(6)$ Å, $c = 13.9964(8)$ Å, $\beta = 101.210(1)°$ for A = Cs), thallium in $K_6NbTlAs_4$ (orthorhombic, $Pnma$, $Z = 4$, $a = 18.786(1)$ Å, $b = 10.4442(4)$ Å, $c = 7.715(1)$ Å), and lead in $K_8NbPbAs_5$ (monoclinic, $C2/c$, $Z = 8$, $a = 31.597(9)$ Å, $b = 9.353(1)$ Å, $c = 13.427(2)$ Å, $\beta = 95.25(1)°$). The lead atom in the latter is bonded to a third arsenic atom as well. Magnetic measurements showed diamagnetic behavior, and therefore, the compounds are electronically balanced, closed-shell type compounds and can be described as transition-metal Zintl phases. The bonding in the anion $NbAs_5^{6-}$ is discussed in detail.

Introduction

Zintl phases containing transition metals are quite rare and involve predominantly elements that can readily achieve either d^0 or d^{10} state. Such elements are the early and late transition metals of groups 4, 5, and 6 as d^0 ions[1] and of groups 10, 11, and 12 as d^{10} ions.[2] These electronic configurations mimic main-group elements, and therefore, the compounds, when electronically balanced, can be considered as Zintl phases.[3] All but two of the compounds with pnictogens (Pn) of transition metals at d^0 state contain isolated tetrahedra MPn_4^{n-} or edge-sharing dimers of tetrahedra $M_2Pn_6^{m-}$ (M = Ti, Hf, Nb, Ta, W).[1] The two exceptions are $Rb_5TaTl_2As_4$, where two opposite edges of the tetrahedral $TaAs_4$ are bridged by thallium atoms,[4] and $Cs_7NbIn_3As_4$, where three edges of the tetrahedral $NbAs_4$ are bridged by indium atoms that are in turn bonded to another arsenic atom forming a cubane-like assembly.[5] These two compounds were accidentally synthesized when trying to make the corresponding Ta- and Nb-free compounds in Ta and Nb containers, respectively, at relatively high temperatures. Our interests went further into exploring this apparent readiness of niobium to react with arsenic and form tetrahedral species, and more extensive and systematic studies of the quaternary systems A−Nb−As−E (A = alkali metal and E = post-transition element) were undertaken. Reported here are three new d^0 transition-metal Zintl phases: A_6NbAs_5 (A = K, Rb, Cs), $K_6TlNbAs_4$, and $K_8PbNbAs_5$. They contain isolated anions made of tetrahedral $NbAs_4$ where one edge is bridged by As, Tl, or Pb(As).

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Experimental Section

Synthesis. All operations were carried out in a N_2-filled glovebox (moisture level below 1 ppm) or under vacuum. Initially synthesized were the isostructural A_6NbAs_5 (A = K, Rb, Cs) found in the products of reactions intended to produce the recently reported binaries A_5As_4 but at higher temperatures.[6] Apparently, as we and others have found, when mixed with alkali metals, arsenic readily attacks the niobium and tantalum containers at temperatures above 600−650 °C. Similarly, $K_6NbTlAs_4$ was initially synthesized from a reaction designed to produce an eventual thallium analogue of the recently reported quaternary $Cs_7NbIn_3As_5$.[5] Finally, $K_8NbPbAs_5$ was made while attempting to substitute lead for thallium in $K_6NbTlAs_4$.

After the compositions of the title compounds were established from the structure determinations, they were synthesized in high yield from the corresponding stoichiometric mixtures of the elements (Cs, 99.95%, and Nb, powder, -325 mesh, 99.8% from Acros; K, 98%, Rb, 99.8%, Pb, 99.9999%, and As sponge, 99.5% from Alfa Aesar). The mixtures were loaded in niobium containers that were then sealed by arc-welding under argon and placed in fused-silica ampules, and the latter were evacuated and flame-sealed. The assemblies were heated at 850 °C for 2 days and were then slowly cooled to room temperature at a rate of 6 °C per hour. All compounds are shiny dark-gray to black and very brittle, exhibit very smooth surfaces, and are very air-sensitive. The crystals have platelike morphology, and some are of relatively large sizes, up to several millimeters.

Structure Determination. Single crystals of all five compounds were mounted in thin-wall glass capillaries and were inspected for singularity on an Enraf-Nonius CAD4 single-crystal diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å). Unit cell parameters were determined for the compounds, and data were collected ($2\theta_{\max} = 50°$, $\omega{-}2\theta$ scans, room temperature) for the best crystals of K_6NbAs_5 ($0.12 \times 0.10 \times 0.10$ mm^3), $K_8NbPbAs_5$ ($0.14 \times 0.06 \times 0.04$ mm^3), and $K_6NbTlAs_4$ ($0.18 \times 0.18 \times 0.04$ mm^3). The structures were solved with direct methods and refined (on F^2) with the SHELXTL-V5.1 software package. According to their symmetry and lattice parameters, Rb_6NbAs_5 and Cs_6NbAs_5 are isostructural with K_6NbAs_5. The refinement of the latter indicated that there were a few closely positioned and partially occupied pairs (K9/K10, K13/K14, and K15/K16) and a triplet (K11/K12/K17) of potassium positions. The sums of the refined occupancies in each pair and the triplet (when freed to vary), however, were very close to 100% and gave a formula of $K_{5.97(4)}NbAs_5$. This and the diamagnetic behavior of the compound (see later) indicated that these were indeed fully occupied but split positions and were refined as such; that is, the occupancy of one of the positions of the split site was freed to vary while the other was added to a full occupancy. Thus, when positions K9, K12, K13, and K15 are occupied, their counterparts K10, K11, K14, K16, and K17 are empty, and vice versa. Nevertheless, to further corroborate these results and to rule out any possible superstructure, data of a single crystal of the cesium analogue Cs_6NbAs_5 were collected on a Bruker APEX diffractometer with a CCD area detector at −133 °C. The cell parameters and choice of space group were confirmed, and furthermore, the refinement of the structure exhibited the same problems with cations Cs9 to Cs17. Again, when the occupancies of these positions were freed to refine, the formula of the compound was virtually the same as for the potassium analogue, $Cs_{5.95(3)}NbAs_5$. In the final refinement, the pairs of positions forming the split sites were constrained to add to a fully occupied site. Details of the data collections and refinements for Cs_6NbAs_5, $K_6NbTlAs_4$, and $K_8NbPbAs_5$ are given in Table 1, while the final positional and equivalent isotropic displacement parameters and important distances are listed in Tables 2 and 3, respectively.

Table 1. Selected Data Collection and Refinement Parameters for Cs_6NbAs_5, $K_6TlNbAs_4$, and $K_8PbNbAs_5$

	Cs_6NbAs_5	$K_6TlNbAs_4$	$K_8PbNbAs_5$
fw	1264.97	831.56	987.50
space group, Z	$P2_1/c$, 8	$Pnma$, 4	$C2/c$, 8
lattice params	$a = 27.405(1)$ Å	$a = 18.786(1)$ Å	$a = 31.597(9)$ Å
	$b = 9.9447(6)$ Å	$b = 10.4442(4)$ Å	$b = 9.353(1)$ Å
	$c = 13.9964(8)$ Å	$c = 7.715(1)$ Å	$c = 13.427(2)$ Å
	$\beta = 101.210(1)°$		$\beta = 95.25(1)°$
	$V = 3741.7(4)$ Å^3	$V = 1513.7(2)$ Å^3	$V = 3951(1)$ Å^3
radiation, λ	Mo Kα, 0.710 73 Å		
temp	−133 °C	20 °C	20 °C
abs coeff	208.91 cm^{-1}	216.71 cm^{-1}	190.58 cm^{-1}
density (calcd)	4.491 g/cm^3	3.649 g/cm^3	3.320 g/cm^3
R1/wR2 ($I > 2\sigma_I$)[a]	5.75/15.25%	3.35/7.13%	6.11/19.36%
R1/wR2 (all data)	7.27/15.97%	4.79/7.62%	8.51/22.97%

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F^2{}_o)^2]\}^{1/2}$ for $F_o{}^2 > 2\sigma(F_o{}^2)$, $w = [\sigma^2(F_o)^2 + (0.0831P)^2 + 79.1799P]^{-1}$ for Cs_6NbAs_5, $w = [\sigma^2(F_o)^2 + (0.0372P)^2]^{-1}$ for $K_6TlNbAs_4$, $w = [\sigma^2(F_o)^2 + (0.1678P)^2]^{-1}$ for $K_8PbNbAs_5$, where $P = [(F_o)^2 + 2(F_c)^2]/3$.

Magnetic Measurements. The magnetizations of 28.5 mg of K_6NbAs_5, 30 mg of $K_6NbTlAs_4$, and 23 mg of $K_8NbPbAs_5$ were measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T over the temperature range 10−250 K. Each sample was sealed in fused silica tubing between two tightly fitting rods of the same material. After correction for the holder and for the ion-core diamagnetism, the molar magnetic susceptibilities of the three compounds were negative and temperature independent: $(-0.85$ to $-1.0) \times 10^{-4}$, $(-0.5$ to $-0.9) \times 10^{-4}$, and $(-0.6$ to $-0.9) \times 10^{-4}$ emu·mol^{-1} for K_6NbAs_5, $K_6NbTlAs_4$, and $K_8NbPbAs_5$, respectively.

Results and Discussion

The structures of the title compounds contain different isolated heteroatomic anions "immersed" in "seas" of alkali metal cations that keep them well separated and balance their charges. Although involving different elements, the three anions of $NbAs_5{}^{6-}$, $TlNbAs_4{}^{6-}$, and $PbNbAs_5{}^{8-}$ are all based on tetrahedrally coordinated Nb(V), [$NbAs_4$], where one of the tetrahedral edges is bridged by another atom or a group. The latter is another arsenic atom in $NbAs_5{}^{6-}$, a thallium atom in $TlNbAs_4{}^{6-}$, and a lead atom that is additionally bonded to a third arsenic in $PbNbAs_5{}^{8-}$ (Figure 1). Thus, the formulas of the anions can be presented as $As_2NbAs_2(\mu\text{-}As)$, $As_2NbAs_2(\mu\text{-}Tl)$, and $As_2NbAs_2[\mu\text{-}Pb(As)]$. The anions are well-separated from each other by $d_{\min}$ of 4.216(3), 4.800(4), and 4.931(2) Å for K_6NbAs_5, $K_6NbTlAs_4$, and $K_8NbPbAs_5$, respectively, and any direct interactions between them are insignificant. (There are two crystallographically different but otherwise isostructural anions in K_6NbAs_5.) Another way to view the geometry of the three anions is to relate them to a cyclobutane-like core with different substituents. Thus, $NbAs_5{}^{6-}$ and $TlNbAs_4{}^{6-}$ are analogous to 1,1-dimethyl cyclobutane while $PbNbAs_5{}^{8-}$ is the analogue of 1,1,3-trimethyl cyclobutane. Taking into account that Nb^+ is isoelectronic with C, As^- and As^{2-} are isoelectronic with CH_2 and CH_3, respectively, and Pb^- is isoelectronic with

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement (Å^2) for Cs_6NbAs_5, $K_6TlNbAs_4$, and $K_8PbNbAs_5$

atom	*x*	*y*	*z*	$U_{eq}{}^{a}$	occup (%)
			Cs_6NbAs_5		
Nb1	0.11815(5)	0.5914(1)	0.3522(1)	0.0135(3)	
Nb2	0.37244(6)	0.8973(1)	0.3450(1)	0.0245(4)	
As1	0.05357(6)	0.5612(1)	0.2061(1)	0.0190(4)	
As2	0.13380(6)	0.8330(1)	0.3830(1)	0.0164(4)	
As3	0.09272(6)	0.4415(1)	0.4882(1)	0.0197(4)	
As4	0.19100(6)	0.4488(1)	0.3180(1)	0.0197(4)	
As5	0.18295(6)	0.4305(1)	0.4891(1)	0.0213(4)	
As6	0.41077(9)	0.6854(2)	0.4154(1)	0.0463(6)	
As7	0.30396(7)	0.8356(1)	0.2180(1)	0.0262(4)	
As8	0.34848(8)	0.0418(2)	0.4821(1)	0.0320(5)	
As9	0.43646(9)	0.0635(2)	0.2947(1)	0.0481(6)	
As10	0.36727(8)	0.1798(2)	0.3480(1)	0.0331(5)	
Cs1	0.26494(4)	0.7287(1)	0.45370(8)	0.0248(3)	
Cs2	0.17064(4)	0.7151(1)	0.64406(7)	0.0219(3)	
Cs3	0.03248(4)	0.5949(1)	0.67403(7)	0.0197(2)	
Cs4	0.01472(4)	0.7995(1)	0.44864(8)	0.0243(3)	
Cs5	0.09452(4)	0.2061(1)	0.29855(8)	0.0263(3)	
Cs6	0.31453(5)	0.0116(1)	0.7432(1)	0.0390(3)	
Cs7	0.14143(5)	0.0963(1)	0.56960(8)	0.0336(3)	
Cs8	0.23518(5)	0.0974(1)	0.3081(1)	0.0540(5)	
Cs9	0.41621(7)	0.6846(3)	0.1510(1)	0.0393(6)	79.7(5)
Cs10	0.4159(3)	0.753(1)	0.1311(6)	0.0393(6)	100-Cs9
Cs11	0.4436(3)	0.3623(9)	0.5189(6)	0.0418(5)	$^2/_3$(100-Cs12)
Cs12	0.46836(6)	0.1694(1)	0.5660(1)	0.0418(5)	76.0(2)
Cs13	0.33730(12)	0.1021(2)	0.0671(1)	0.0515(7)	75.5(4)
Cs14	0.3118(4)	0.1315(8)	0.0846(6)	0.0515(7)	100-Cs13
Cs15	0.47953(8)	0.4151(2)	0.3582(1)	0.0592(6)	78.5(2)
Cs16	0.4603(3)	0.4004(7)	0.2466(7)	0.0592(6)	100-Cs15
Cs17	1/2	0	1/2	0.0418(5)	$^1/_3$(100-Cs12)
			$K_6TlNbAs_4$		
Tl	0.44879(3)	1/4	0.93594(7)	0.0290(1)	
Nb	0.32987(6)	1/4	0.6060(1)	0.0170(3)	
As1	0.33009(9)	1/4	0.2887(1)	0.0260(3)	
As2	0.20454(8)	1/4	0.7083(1)	0.0242(3)	
As3	0.39804(6)	0.05538(8)	0.7143(1)	0.0225(2)	
K1	0.5047(2)	1/4	0.4412(5)	0.054(1)	
K2	0.2572(1)	0.0452(1)	0.9953(2)	0.0278(5)	
K3	0.4217(1)	0.9819(2)	0.2173(4)	0.0475(7)	
K4	0.6508(2)	1/4	0.1808(4)	0.0422(9)	
			$K_8PbNbAs_5$		
Pb	0.40981(2)	0.11545(8)	0.46478(6)	0.0180(3)	
Nb	0.34315(5)	0.3398(1)	0.3184(1)	0.0116(4)	
As1	0.35849(7)	0.5957(2)	0.3510(1)	0.0169(5)	
As2	0.28444(7)	0.3141(2)	0.1858(1)	0.0192(5)	
As3	0.32370(7)	0.2039(2)	0.4733(1)	0.0172(5)	
As4	0.40711(7)	0.2072(2)	0.2629(1)	0.0179(5)	
As5	0.47113(7)	0.2582(2)	0.5782(1)	0.0207(5)	
K1	0.5193(1)	0.1191(5)	0.3911(4)	0.032(1)	
K2	0.2656(1)	0.5403(5)	0.4468(4)	0.028(1)	
K3	0.3850(1)	0.4609(5)	0.6010(4)	0.028(1)	
K4	0.2242(1)	0.1554(5)	0.3320(4)	0.027(1)	
K5	0.3235(1)	0.9586(5)	0.2816(4)	0.034(1)	
K6	0.3506(1)	0.1693(5)	0.0402(4)	0.030(1)	
K7	0.4601(1)	0.4751(5)	0.3796(4)	0.032(1)	
K8	0.5641(1)	0.1688(5)	0.7094(4)	0.028(1)	

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

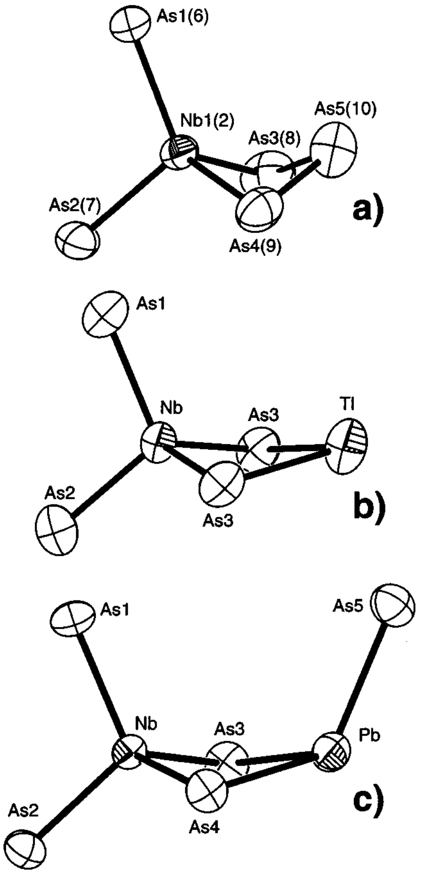

Figure 1. ORTEP drawings (thermal ellipsoids at the 90% probability level) of the anions in (a) Cs_6NbAs_5 (the numbers in parentheses are for the second isostructural anion in the same compound, see the text), (b) $K_6TlNbAs_4$, and (c) $K_8PbNbAs_5$. The bending of the four-membered rings along the As···As diagonal (measured by the corresponding dihedral angles) are 126.4(1)° and 122.4(1)° for the two anions of $NbAs_5{}^{6-}$ in Cs_6NbAs_5, (123.1(1)° and 121.4(1)° in K_6NbAs_5), 152.24(8)° for $TlNbAs_4{}^{6-}$, and 151.2(1)° for $PbNbAs_5{}^{8-}$.

Table 3. Important Distances (Å) and Angles (deg) in $[NbAs_5]^{6-}$, $[NbAs_4Tl]^{6-}$, and $[NbAs_4PbAs]^{8-}$

$[NbAs_5]^{6-}$		$[NbAs_4Tl]^{6-}$	
Nb1−As1	2.449(2)	Nb−As1	2.448(1)
Nb1−As2	2.463(2)	Nb−As2	2.483(1)
Nb1−As3	2.617(2)	Nb−As3	2.543(1)2×
Nb1−As4	2.569(2)	Nb−Tl	3.386(1)
Nb1−As5	2.839(2)	Tl−As3	2.822(1)2×
As3−As5	2.473(2)		
As4−As5	2.454(2)	As3−Nb−As3	106.10(6)
Nb2−As6	2.472(2)	As3−Tl−As3	92.14(4)
Nb2−As7	2.400(2)	Nb−As3−Tl	78.08(3)
Nb2−As8	2.583(2)	$[NbAs_4PbAs]^{8-}$	
Nb2−As9	2.604(2)	Nb−As1	2.474(3)
Nb2−As10	2.814(2)	Nb−As2	2.463(3)
As8−As10	2.460(2)	Nb−As3	2.559(3)
As9−As10	2.458(3)	Nb−As4	2.540(3)
		Nb−Pb	3.456(1)
As3−Nb1−As4	98.50(7)	Pb−As3	2.856(2)
As3−As5−As4	105.76(8)	Pb−As4	2.837(2)
Nb1−As3−As5	67.75(7)	Pb−As5	2.705(2)
Nb1−As4−As5	68.80(7)		
As8−Nb2−As9	97.44(9)	As3−Nb−As4	104.64(9)
As8−As10−As9	104.9(1)	As3−Pb−As4	90.29(6)
Nb2−As8−As10	67.79(8)	Nb−As3−Pb	79.10(7)
Nb2−As9−As10	67.48(8)	Nb−As4−Pb	79.78(7)

CH, we can easily determine the charges of $NbAs_5$ and $PbNbAs_5$ as 6− and 8−, respectively. Thus, the former is $(As^{2-})_2(Nb^+)(As^-)_3$ while the latter is $(As^{2-})_2(Nb^+)(As^-)_2(Pb^-)(As^{2-})$. The anion $TlNbAs_4$ is a special case where Tl^- should be considered as the planar isolobal analogue (derived from planar TlH_3) of CH_2 (derived from tetrahedral CH_4). Planar Tl^- satisfies a sextet rule (with an empty p_z orbital) instead of the octet rule for atoms with nonplanar coordination exactly in the same way as square-planar transition-metal complexes satisfy the 16-electron rule (with an empty p_z orbital) instead of the 18-electron rule for nonplanar compounds. Thus, the charge of 6− of this anion can be expressed as $(As^{2-})_2(Nb^+)(As^-)_2(Tl^-)$. All these charges are, of course, not real charges on the atoms but are rather formalism for rationalizing the overall charges of the anions. The latter are derived on the basis of the numbers of available cations per anion assuming complete electron transfer. This is in agreement with the observation that the compounds are diamagnetic, that is, electronically balanced compounds, on the basis of their negative magnetic susceptibility.

Another, perhaps more readily accepted way to account for the charges of the anions is to consider niobium as Nb(V), lead as Pb(II), thallium as Tl(I), and arsenic as isolated As^{3-} anions and an As_3^{5-} trimer. This view, however, diminishes somewhat the covalency of the bonding within the aggregates and puts more importance on donor−acceptor and ionic interactions. Nevertheless, using this method, the corresponding heteroatomic anions can be written as $(As^{3-})_2(Nb^{5+})(As_3^{5-})$, $(As^{3-})_2(Nb^{5+})(As^{3-})_2(Tl^{+})$, and $(As^{3-})_2(Nb^{5+})(As^{3-})_2(Pb^{2+})(As^{3-})$. It should be pointed out that the pairs of s electrons on thallium and lead are recognized as inert and the two ions are considered as mono- and dications, respectively. This approach for thallium was used previously in the rationalization of the charge of $Tl_2TaAs_4^{5-}$ where two opposite edges of the $TaAs_4$ tetrahedron are bridged by thallium atoms, $(Tl^{+})(As^{3-})_2$-$Ta(As^{3-})_2(Tl^{+})$.[4]

The Nb−As distances in the anions are of two types. Those involving terminal arsenic are quite short and fall in the range 2.400(3)−2.483(1) Å. They are somewhat shorter than the distances in the isolated tetrahedra of $NbAs_4^{7-}$ found in $Na_5SrNbAs_4$ and $K_5BaNbAs_4$, 2.480(4)−2.503(1) Å, and in K_7NbAs_4 and Rb_7NbAs_4, 2.487(2)−2.519(4) Å.[1b,c] This is quite predictable considering that all four arsenic atoms in the isolated tetrahedra can π-interact with the empty d orbitals of the central niobium atom while only two such atoms, the terminal ones, are capable of doing that in the anions discussed here. Thus, these d orbitals provide bonding to only two atoms in the latter case, and obviously, this should lead to shorter distances. Molecular orbital analysis has shown that the bond order in an isolated tetrahedron is 2.25 per bond with nine bonding molecular orbitals (each ligand participates with two tangential p orbitals) distributed among four bonds.[7] The same study assigns bond order of 3.00 for the bonds to the two terminal arsenic ligands in tetrahedra where the other two ligands are not capable of π-bonding. Somewhere between these two extremes is the case of the anions discussed here because the two-bonded arsenic atoms of the four-membered rings might have some π-bonding capabilities. The lower limit of the range of distances to terminal arsenic atoms in these anions, 2.400(3) Å (Table 3), is virtually equal to the triple-bond distance of 2.390(2) Å observed in $[In_3As_4Nb{\equiv}As]^{7-}$, a cubane of In_3As_4Nb with a handle of arsenic bonded to the niobium corner.[5] It should be mentioned here that 2.720(1) Å is the single-bond Nb−As distance observed in $(Cp)_2(H_2)Nb{-}AsEt_2$, a dihidroarsenido derivative of niobocene.[8]

The second type of Nb−As distance is the distance to two-bonded arsenic atoms, those of the four-membered rings, and these range from 2.540(3) to 2.617(2) Å. These distances are substantially longer than the distances in the isolated tetrahedra mentioned previously but, on the other hand, are quite shorter than the single-bond distance of 2.720(1) Å.[8] As already discussed, these atoms are capable of some limited π-bonding with the niobium.

In addition to the Nb−As bonds, there are also bonds between the bridging atom and arsenic, that is, As−As, Tl−As, and Pb−As in $NbAs_5^{6-}$, $NbTlAs_4^{6-}$, and $PbNbAs_5^{8-}$, respectively. The only other example of Tl−As bond is found in the anion $Tl_2TaAs_4^{5-}$ where two opposite edges of the tetrahedral $TaAs_4$ are bridged by thallium.[4] The three different Tl−As distances observed in this anion, 2.883(8), 2.8015(5), and 2.739(7) Å, compare well with 2.822(1) Å observed in $TlNbAs_4^{6-}$ with one bridged edge. One can view the latter also as niobium(V) coordinated by two isolated arsenic ligands of As^{3-} and a bidentate ligand of $[As{-}Tl{-}As]^{5-}$. The inertness of the s-pair at thallium is manifested by the very close to 90° angle at that atom, 92.14(4)° (Table 3), which indicates lack of s−p hybridization. Similar is the situation at the lead atom of $PbNbAs_5^{8-}$ where the angle involving the two-bonded arsenic atoms is 90.29(6)° (Table 3). This anion, to the best of our knowledge, is the first species with bonds between lead and arsenic. The bonds to the two-bonded arsenic atoms are longer, 2.856(2) and 2.837(2) Å, than that to the terminal arsenic, 2.705(2) Å. Because there are no other compounds with Pb−As bonds, these three distances can only be rationalized by comparing them with sums of radii from other compounds. Thus, similar three-bonded lead atoms are found in the structure of NaPb with isolated tetrahedra of Pb_4^{4-},[9] and two-bonded arsenic atoms are found in the helical chains of $({-}As^{-}{-})_\infty$ in KAs.[10] The sum of the halves of the average Pb−Pb distance of 3.16 Å in the tetrahedron and of the average As−As distance of 2.49 Å in the chains, 2.825 Å, provides a reasonable Pb−As distance. This value compares very well with the distances to the two-bonded arsenic atoms of $PbNbAs_5^{8-}$. Another species, a tetramer of arsenic in K_5As_4, can be used to estimate a radius for a terminal arsenic by subtracting the already determined radius for two-bonded arsenic from the terminal distance of 2.424 Å in the tetramer.[6] This radius, 1.179 Å, summed with that for the three-bonded lead, provides 2.759 Å for the Pb−As distance which also compares well with the observed 2.705(2) Å (Table 3). The shortening may also be due to p_π-d_π interactions of the filled arsenic 4p orbitals and the empty lead 6d orbitals. Again, the anion can be considered as niobium(V) coordinated by two isolated As^{3-} ligands and a bidentate ligand of $[As{-}Pb(As){-}As]^{7-}$

Next, we focus our attention exclusively on the bonding in the arsenic-bridged anion $NbAs_5^{6-}$. It has two As−As bonds with distances of 2.473(2) and 2.454(2) Å in one of the two isostructural but crystallographically different anions

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and of 2.460(2) and 2.458(3) Å in the other one. These distances compare very well with the average distance of 2.490 Å for two-bonded arsenic atoms in the helical chains in KAs.[10] The anion can be viewed as niobium(V) coordinated by two single arsenic ligands As^{3-} and a bidentate trimer of $[As{-}As{-}As]^{5-}$ (Figure 1). The latter, however, is positioned somewhat differently than the corresponding bidentate $[As{-}Tl{-}As]^{5-}$ and $[As{-}Pb(As){-}As]^{7-}$ discussed previously. It is close to being coordinated sidewise to the niobium acting almost as a tridentate ligand according to the Nb−As distance to the middle arsenic, 2.814(2) and 2.839(2) Å in the two anions. This is not much longer than the single-bond Nb−As distance of 2.720 Å and indicates clearly some bonding interactions. The latter are also strongly manifested by the small dihedral angle along the As···As diagonal of the four-membered ring, 126.4(1)° and 122.4(1)° for the two independent anions (123.1(1)° and 121.4(1)° in K_6NbAs_5). The corresponding rings in $TlNbAs_4^{6-}$ and $PbNbAs_5^{8-}$ are considerably flatter with dihedral angles of 152.24(8)° and 151.2(1)°, respectively. Furthermore, the bending in $NbAs_5^{6-}$ caused by the Nb···As interactions across the ring apparently overcomes the counteracting strain of the resulting very small angles at the arsenic atoms of the bending axis. Thus, the average Nb−As−As angle at these atoms is 68° while the average Nb−As−Tl and Nb−As−Pb angles are 78° and 79°, respectively. This is also corroborated by extended Hückel molecular orbital calculations of the anion which gave the following bond-overlap populations for the different Nb−As bonds: 1.23 to the terminal arsenic, 0.77 to the two-bonded arsenic, and 0.23 to the arsenic atom in question. The latter is definitely substantial compared to the other two numbers which correspond to multiple bonding as discussed previously.

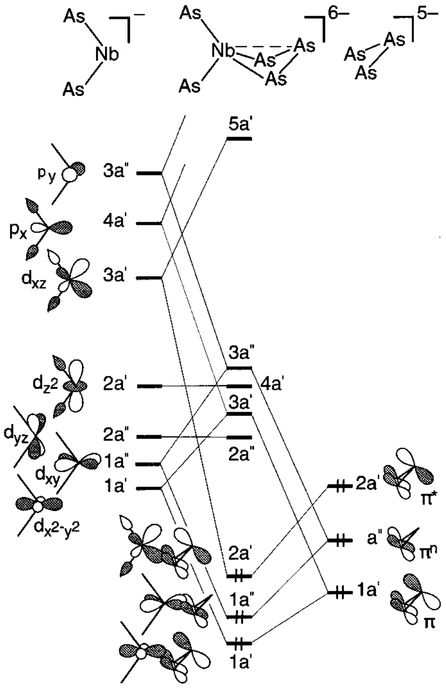

Figure 2. Orbital interaction diagram for $NbAs_5^{6-}$ made of the fragments As_2Nb^- and bent $[As{-}As{-}As]$.$^{5-}$ Only the frontier orbitals for the two fragments are shown. The orbitals of As_2Nb^- are labeled assuming vertical z and horizontal x axes, while the p_z orbitals of As_3^{5-} are perpendicular to the plane of the trimer.

Molecular orbital analysis of $NbAs_5^{6-}$ (Figure 2) indicates that the Nb−As interactions across the ring involve predominantly the empty d_{xz} and $d_{x^2-y^2}$ orbitals at niobium and the p orbital at the arsenic that is perpendicular to the plane of the arsenic trimer. The latter is a part of the filled π-system of the trimer made of the p_z orbitals. The MO developed from the frontier orbitals of the two fragments As_2Nb^- and the bent $[As{-}As{-}As]^{5-}$ is shown in Figure 2. The ML_2 fragment can be easily derived from the MO diagram of a square-planar ML_4 by removing two of the ligands.[11] For Nb(V), these predominantly metal-based non- and antibonding d and p orbitals are empty. The frontier orbitals of the bent trimer are also easily envisioned as the π-system of the isostructural allyl where the three combinations of bonding, nonbonding, and antibonding interactions are all filled. All three π-orbitals of the trimer have appropriate matches with the ML_2 fragment and form three bonding orbitals with $d_{x^2-y^2}$ (mixed with p_x), d_{xy} (mixed with p_y), and d_{xz}. However, only two of these interactions, those with d_{xz} and to some extent with $d_{x^2-y^2}$, involve the middle atom of the trimer. Thus, based purely on this MO diagram, that is, not considering the underlying σ- and π-bonding Nb−As molecular orbitals for the two end-atoms of the trimer, the Nb−As bond orders for the end- and middle-arsenic atoms can be calculated as 1.167 ($^7/_6 = {}^1/_3$ 1a′ + $^1/_2$ 1a″ + $^1/_3$ 2a′; these are fractions of each occupied MO that contribute to bonding per Nb−As bond to terminal atom, see Figure 2) and 0.667 ($^2/_3 = {}^1/_3$ 1a′ + $^1/_3$ 2a′; these are fractions of each occupied MO that contribute to the Nb−As bond to the middle arsenic atom of the trimer, see Figure 2), respectively. The latter correlates very well with the Nb−As distance of 2.839(2) Å (2.814(2) Å in the second anion) to the middle arsenic atom when compared with the distance for bond order of 1, that is, the single-bond distance of 2.720 Å.[8] According to Pauling's relation between bond order and distance, $d_n = d_1 - 0.6 \log(n)$ where d_n and d_1 are distances for bond orders n and 1, the distance for bond order 0.667 is 2.825 Å (assuming $d_1 = 2.720$ Å).[12] It should be pointed out that these Nb−As distances across the ring compare well also with those of four-bonded arsenic in various phenyldimethylarsine complexes of niobium, 2.669−2.745 Å,[13] as well as with the distances in $(Cp^*)(CO)_2Nb(\eta^4\text{-}As_4)$, 2.716−2.766 Å, where one of the ligands is a square of arsenic.[14]

The same fragment orbital interactions can be developed for the thallium anion between As_2Nb^- and the bent $[As{-}Tl{-}As]$.$^{5-}$ However, the π^* orbital of the trimer is empty in this case because the p_z of thallium is empty, and therefore,

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only two of the bonding orbitals for the corresponding complete anion (Figure 2) are occupied. This leads to much smaller bond order for the Nb−Tl interactions and consequently to much longer distance and less bent four-membered ring. The lead atom in $PbNbAs_5^{8-}$, on the other hand, does not even have an available p_z orbital because it is already used for the additional Pb−As bond to the third (terminal) arsenic, and the lone pair of electrons at the lead atom is predominantly of s character (inert-pair effects).

These three niobium-based compounds add three more examples to the rapidly growing class of transition-metal Zintl phases. Even more interesting compounds with mixed-valent or reduced transition metals with partially filled d orbitals such as the known $(AE)_{14}MnPn_{11}$ (AE = alkaline-earth) and $Sr_{21}Mn_4Sb_{18}$ can be expected from these systems as well.[3,15]

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Supporting Information Available: X-ray crystallographic file for Cs_6NbAs_4, $K_6TlNbAs_4$, $K_8PbNbAs_5$, and K_6NbAs_5 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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