Synthesis and Characterization of the "Metallic Salts" A_5Pn_4 (A = K, Rb, Cs and Pn = As, Sb, Bi) with Isolated Zigzag Tetramers of Pn_4^{4-} and an Extra Delocalized Electron

Franck Gascoin and Slavi C. Sevov*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received April 27, 2001

The isostructural title compounds were prepared by direct reactions of the corresponding elements, and their structures were determined from single-crystal X-ray diffraction data in the monoclinic space group *C*2/*m*, *Z* = 2 (K_5As_4, *a* = 11.592(2) Å, *b* = 5.2114(5) Å, *c* = 10.383(3) Å, β = 113.42(1)°; K_5Sb_4, *a* = 12.319(1) Å, *b* = 5.4866(4) Å, *c* = 11.258(1) Å, β = 112.27(7)°; Rb_5Sb_4, *a* = 12.7803(9) Å, *b* = 5.7518(4) Å, *c* = 11.6310(8) Å, β = 113.701(1)°; K_5Bi_4, *a* = 12.517(2) Å, *b* = 5.541(1) Å, *c* = 11.625(2) Å, β = 111.46(1)°; Rb_5Bi_4, *a* = 12.945(4) Å, *b* = 5.7851(9) Å, *c* = 12.018(5) Å, β = 112.78(3)°; Cs_5Bi_4, *a* = 12.887(3) Å, *b* = 6.323(1) Å, *c* = 12.636(1) Å, β = 122.94(2)°). The compounds contain isolated and flat zigzag tetramers of Pn_4^{4-} (Pnictide (Pn) = As, Sb, Bi) with a conjugated π-electron system of delocalized electrons. All six compounds are metallic ("metallic salts") and show temperature-independent (Pauli-like) paramagnetism due to a delocalized electron from the extra alkali-metal cation in the formula. At low temperatures (around 9.5 K) and low magnetic fields the bismuthides become superconducting.

Introduction

Over the past decade, solid-state reactions between alkali metals and post-transition elements have led to the discovery of many new compounds with a variety of novel features. Surprisingly, even simple binary systems, generally thought to have been already exhaustively studied, have shown unexpected richness in the numbers of new compounds found in them. This is illustrated well by the numerous recently discovered binary compounds of the heavier elements of groups 13 (Ga, In, and Tl) and 14 (Si, Ge, Sn, and Pb) with the alkali metals.[1,2] They contain a variety of previously unknown "naked" clusters with negative charges and delocalized bonding such as In_{11}^{7-}, Tl_6^{6-}, Tl_{13}^{11-}, Ge_9^{4-}, Si_9^{4-}, Ge_{12}^{12-}, etc. On the other hand, formation of such or similar anionic deltahedral clusters of the pnictogens (Pn) is very unlikely because they are electron-rich elements that do not need to "share" electrons for effective bonding. Instead, they usually form extended structures with "normal" two-center-two-electron bonds such as oligomers, chains, layers, and frameworks. Recently, we reported the synthesis and characterization of such an oligomeric species in the system alkali-metal−bismuth, A_3Bi_2, with isolated dimers of Bi_2^{2-}.[3] The three available alkali-metal cations of the formula provide an extra electron, which delocalizes over the dimers and the cations and makes metallic the otherwise saltlike compound; in other words, a "metallic salt" is formed.[3] Furthermore, K_3Bi_2 dissolves in ethylenediamine and in the presence of crypt (crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane), the electron-balanced compound (K-crypt)$_2Bi_2$ with a double-bonded dianion $[Bi_2]^{2-}$, isoelectronic with O_2, can be crystallized.[4] Also, bent trimers of $[Bi_3]^{3-}$, isoelectronic with ozone, O_3, can be "fished out" from such solutions with the help of (mesitylene)M(CO)$_3$ (M = Cr or Mo), which is used as the "bait". They form heteroatomic transition-metal-main group closo-clusters of $[Bi_3M_2(CO)_6]^{3-}$.[5] These bismuth species in the A_3Bi_2 precursors and in the compounds crystallized from their solutions present multiple Bi−Bi bonding. Here, we report the syntheses and characterizations of the compounds K_5As_4, A_5Sb_4 (A = K, Rb), and A_5Bi_4 (A = K, Rb, Cs) with even larger pnictide oligomers, zigzag tetramers of Pn_4^{4-}, and also multiple bonding.[6] Similar to A_3Bi_2, they also belong to the class of "metallic salts" due to the extra alkali-metal cation and the corresponding "extra" electron delocalized over the structure.

Experimental Section

Synthesis. All operations were carried out in a N_2-filled glovebox with the moisture level below 1 ppm. Initially, A_5Pn_4 were synthesized from equimolar reactions in an attempt to prepare a precursor for the $[Bi_2]^{2-}$ molecule.[4] Later, stoichiometric mixtures of the elements (Cs (99.95%) from Acros; K (98%), Rb (99.8%), As (99.5%), Sb (99.999%), and Bi (99.999%) all from Alfa-Aesar) were loaded in niobium containers that were then sealed by arc welding under argon and were enclosed in fused silica ampules that were in turn evacuated and flame-sealed. The reaction mixtures were heated at 700 °C for 2 days and then slowly cooled to room temperature at a rate of 5 °C h^{-1}. All compounds are dark gray and brittle but shiny with metallic luster.

* To whom correspondence should be addressed.

(1) Reviews: (a) Corbett, J. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 670. (b) Corbett, J. D. *Struct. Bonding (Berlin)* **1997**, *87*, 157. (c) Corbett, J. D. *Inorg. Chem.* **2000**, *39*, 5178.

(2) (a) Quéneau, V.; Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1754. (b) Quéneau, V.; Sevov, S. C. *Inorg. Chem.* **1998**, *37*, 1358. (c) Quéneau, V.; Todorov, E.; Sevov, S. C. *J. Am. Chem. Soc.* **1998**, *120*, 3263. (d) Todorov, E.; Sevov, S. C. *Inorg. Chem.* **1998**, *37*, 3889. (e) Bobev, S.; Sevov, S. C. *Angew. Chem., Int. Ed.* **2000**, *39*, 4108. (f) Bobev, S.; Sevov, S. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 1507.

(3) Gascoin, F.; Sevov, S. C. *J. Am. Chem. Soc.* **2000**, *122*, 10251.

(4) Xu, L.; Bobev, S.; El-Bahraoui, J.; Sevov, S. C. *J. Am. Chem. Soc.* **2000**, *122*, 1838.

(5) Xu, L.; Ugrinov, A.; Sevov, S. C. *J. Am. Chem. Soc.* **2001**, *123*, 4091.

(6) (a) Some of the A_5Pn_4 compounds were proposed based on phase diagram studies: Dorn, F. W.; Klemm, W.; Lohmeyer, S. *Z. Anorg. Allg. Chem.* **1961**, *309*, 181−204. (b) A structural report on K_5Sb_4 with the tetramers labeled as Sb_4^{5-}, without any comments or discussion, can be found in the following structure report: Somer, M.; Hartweg, M.; Peters, K.; von Schnering, H. G. *Z. Kristallogr.* **1991**, *195*, 103.

10.1021/ic0104499 CCC: $20.00
Published on Web 08/24/2001

Table 1. Crystallographic Data for K_5As_4, K_5Sb_4, Rb_5Sb_4, K_5Bi_4, Rb_5Bi_4, and Cs_5Bi_4 [a]

	K_5As_4	K_5Sb_4	Rb_5Sb_4	K_5Bi_4	Rb_5Bi_4	Cs_5Bi_4
fw	495.18	682.50	914.35	1031.42	1263.27	1500.47
a (Å)	11.592(2)	12.319(1)	12.7803(9)	12.517(2)	12.945(4)	12.887(3)
b (Å)	5.2114(5)	5.4866(4)	5.7518(4)	5.541(1)	5.7851(9)	6.323(1)
c (Å)	10.383(3)	11.258(1)	11.6310(8)	11.625(2)	12.018(5)	12.636(3)
β (deg)	113.42(1)	112.27(7)	113.701(1)	111.46(1)	112.78(3)	122.94(3)
V (Å^3)	575.6(2)	704.2(1)	782.8(1)	750.4(2)	829.8(4)	864.1(3)
ρ_{calc} (g cm^{-3})	2.857	3.219	3.881	4.565	5.056	5.767
μ (cm^{-1})	132.49	90.12	222.35	480.95	568.11	509.42
R1/wR2[b]	0.032/0.073	0.045/0.110	0.030/0.099	0.078/0.197	0.051/0.139	0.089/0.219

[a] For all compounds: $\lambda = 0.710\ 73$ Å (Mo Kα), monoclinic $C2/m$, $Z = 2$; $T = 293$ K for all except Rb_5Sb_4 for which $T = 250$ K. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{[\sum w[(F_o)^2 - (F_c)^2]^2]/[\sum w(F^2_o)^2]\}^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$, $w = [\sigma^2(F_o)^2 + (AP)^2]^{-1}$ where $P = [(F_o)^2 + 2(F_c)^2]/3$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for K_5As_4, K_5Sb_4, Rb_5Sb_4, K_5Bi_4, Rb_5Bi_4, and Cs_5Bi_4

atom	x	y	z	U_{eq}	atom	x	y	z	U_{eq}
		K_5As_4					K_5Bi_4		
As1	0.09602(8)	0	0.10741(9)	0.0202(3)	Bi1	0.1119(1)	0	0.1119(1)	0.0318(9)
As2	0.04276(8)	0	0.31080(9)	0.0221(3)	Bi2	0.0457(1)	0	0.3350(1)	0.0339(9)
K1	0.3906(2)	0	0.0996(2)	0.0242(6)	K1	0.4035(9)	0	0.109(1)	0.035(3)
K2	0.2464(2)	0.5	0.3324(2)	0.0300(5)	K2	0.244(1)	0.5	0.332(1)	0.048(3)
K3	0.023(1)	0.5	0.518(2)	0.047(4)	K3	0	0.5	0.5	0.12(1)
		K_5Sb_4					Rb_5Bi_4		
Sb1	0.1051(1)	0	0.1094(1)	0.0258(4)	Bi1	0.10893(8)	0	0.1128(1)	0.0306(5)
Sb2	0.0440(1)	0	0.3240(1)	0.0274(4)	Bi2	0.04725(9)	0	0.3283(1)	0.0339(5)
K1	0.3970(3)	0	0.1068(4)	0.031(1)	Rb1	0.4011(2)	0	0.1063(3)	0.0333(7)
K2	0.2459(3)	0.5	0.3338(4)	0.036(1)	Rb2	0.2468(2)	0.5	0.3310(3)	0.0453(9)
K3	0.022(7)	0.5	0.51(1)	0.07(1)	Rb3	0.0374(8)	0.5	0.522(1)	0.065(4)
		Rb_5Sb_4					Cs_5Bi_4		
Sb1	0.10179(4)	0	0.11056(4)	0.0249(1)	Bi1	0.1080(2)	0	0.1366(2)	0.0326(8)
Sb2	0.04299(4)	0	0.31800(4)	0.0274(2)	Bi2	0.0009(2)	0	0.2938(2)	0.0282(8)
Rb1	0.39354(6)	0	0.10149(6)	0.0281(2)	Cs1	0.3629(4)	0	0.0542(4)	0.030(1)
Rb2	0.24667(7)	0.5	0.33398(7)	0.0368(2)	Cs2	0.2320(4)	0.5	0.3468(4)	0.037(1)
Rb3	0.0353(2)	0.5	0.5211(3)	0.058(1)	Cs3	0.031(1)	0.5	0.523(1)	0.049(4)

Table 3. Selected Interatomic Distances (Å) and Angles (deg) in K_5As_4, K_5Sb_4, Rb_5Sb_4, K_5Bi_4, Rb_5Bi_4, and Cs_5Bi_4

	K_5As_4	K_5Sb_4	Rb_5Sb_4	K_5Bi_4	Rb_5Bi_4	Cs_5Bi_4
Pn1−Pn1	2.446(2)	2.818(3)	2.8292(9)	3.046(3)	3.063(2)	3.036(5)
Pn2	2.424(1)	2.789(1)	2.8006(7)	2.998(2)	2.992(1)	2.972(3)
A1	3.448(2)	3.607(4)	3.7724(9)	3.665(8)	3.813(3)	3.950(4)
2 x A1	3.420(1)	3.661(3)	3.8047(6)	3.740(6)	3.879(2)	4.115(3)
2 x A1	3.509(1)	3.747(3)	3.8909(6)	3.795(5)	3.931(2)	4.180(3)
2 x A2	3.471(1)	3.687(3)	3.8189(6)	3.723(8)	3.853(2)	3.871(3)
Pn2−2 x A1	3.410(1)	3.665(3)	3.7939(6)	3.780(6)	3.893(2)	4.058(3)
A2	3.530(2)	3.715(4)	3.8553(9)	3.774(9)	3.906(3)	3.871(5)
A2	3.535(3)	3.739(5)	3.8655(9)	3.80(1)	3.918(4)	3.934(5)
2 x A2	3.463(1)	3.677(3)	3.8331(6)	3.721(6)	3.868(2)	4.141(3)
2 x A3	3.41(2)	3.53(8)	3.748(2)	3.41(1)	3.746(8)	4.07(1)
2 x A3	3.44(1)	3.57(8)	3.779(2)	3.67(1)	3.784(8)	4.16(1)
Pn2−Pn1−Pn1	109.85(6)	107.30(7)	108.42(3)	106.30(8)	107.66(6)	106.7(1)

Powder diffraction (Enraf-Nonius Guinier camera with single-crystal monochromated Cu $K\alpha_1$) was used for phase analysis of the products. Pure phases were obtained only for the antimonides and the arsenide, while for the bismuthides, traces of the very stable Laves phase ABi_2 were always present. The latter forms as very fine powder, and usually it is quite easy to separate it from the well-crystallized A_5Bi_4 phases.

Structure Determination. Single crystals of the six compounds were mounted in glass capillaries, using a drybox equipped with a microscope, and were inspected for singularity on an Enraf-Nonius CAD4 single-crystal diffractometer (Mo Kα radiation, $\lambda = 0.71\ 073$ Å). Data were collected at room temperature on the same diffractometer ($2\theta_{max} = 50°$) for all except Rb_5Sb_4 for which data sets were collected at 250 and 140 K on a Bruker APEX diffractomer with a CCD area detector ($2\theta_{max} = 56°$). The structures were solved and refined (after absorption corrections using Xabs or SADABS) in the monoclinic $C2/m$ with the aid of the SHELXTL V5.1 software package (Table 1).[7] The crystals of K_5As_4 (0.24 × 0.20 × 0.20 mm), K_5Sb_4 (0.08 × 0.08 × 0.04 mm), Rb_5Sb_4 (0.10 × 0.10 × 0.04 mm), and Rb_5Bi_4 (0.10 × 0.10 × 0.10 mm) were of very good quality while the crystals of Cs_5Bi_4 (0.12 × 0.08 × 0.08 mm) and K_5Bi_4 (0.14 × 0.12 × 0.10 mm) were considerably worse and diffracted poorly. This and some notable absorption problems for the latter two are reflected in the final residuals (Table 1). The final positional and equivalent isotropic displacement parameters and selected distances for the refined structures are listed in Tables 2 and 3, respectively. There are two positions for the pnictogens, Pn1 and Pn2, and three positions for the alkali metals, A1, A2, and A3. Atom A3 is at a special position with a mirror plane symmetry (m) but is also very close to the 2-fold axis perpendicular to the mirror plane (and the created inversion center, $2/m$) and to the generated equivalent atom, and therefore, it is refined as a statistically exactly half-occupied split position. For K_5Bi_4, however, this splitting is so small that the atom was refined at the $2/m$ position as fully occupied but with a relatively elongated thermal ellipsoid.

(7) (a) Xabs: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158. (b) *SADABS and SHELXTL*, version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

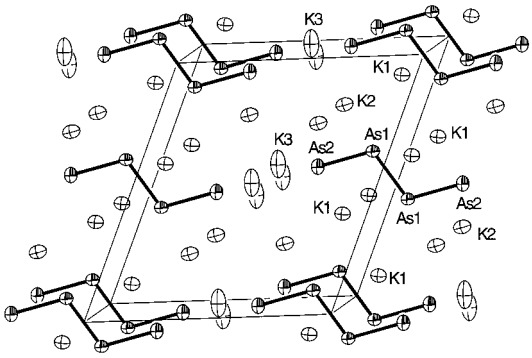

Figure 1. ORTEP drawing of the structure of K_5As_4 as a representative of the isostructural compounds A_5Pn_4 (70% probability for the thermal ellipsoids). The pnictide tetramers are planar with zigzag shape, and the outside distances Pn1−Pn2 are slightly shorter than the inside distance Pn1−Pn1. The tetramers are very well separated by the alkali-metal cations. The position A3 (K3 in this case), for all but K_5Bi_4, is refined as split around an inversion center (as shown in the figure) and is 50% occupied. The view is along the *b*-axis with *c*-horizontal, and the unit cell (monoclinic) is outlined.

Magnetic Measurements. The magnetizations of K_5As_4, K_5Sb_4, Rb_5Sb_4, and K_5Bi_4 were measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T over the temperature range of 10−250 K. Typically, 30−50 mg of a sample are sealed in a fused silica tubing between two tightly fitting rods of the same material. Corrections were applied for the holder and the ion-core diamagnetism. Above 10 K the molar magnetic susceptibilities of the arsenide and the bismuthide are positive, temperature independent, and range between $+(4.2-4.4) \times 10^{-4}$ and $+(2.8-3.0) \times 10^{-4}$ emu mol^{-1}, respectively. The molar susceptibilities of the two antimonides are also positive throughout the whole temperature range but are temperature independent only above 110 K for K_5Sb_4 and 190 K for Rb_5Sb_4 and range between $+(4.4-4.6) \times 10^{-4}$ and $+(2.3-2.4) \times 10^{-4}$ emu mol^{-1}, respectively. Below these temperatures, however, the susceptibilities of both compounds decrease smoothly in a large temperature range. This is independent of whether the samples are cooled with or without magnetic field as well as whether they are going up or down in temperature. The magnetizations of all four compounds indicate metallic behavior at room temperature, and this was confirmed by simple two-probe resistivity tests performed on large crystals of each compound.

Motivated by the fact that many bismuth-based intermetallics become superconducting at low temperatures,[8] we also measured the magnetizations of field-cooled (FC) and zero-field-cooled (ZFC) samples of K_5Bi_4, Rb_5Bi_4, and the previously reported K_3Bi_2[4] at low magnetic fields and temperatures. All samples showed superconducting transitions within the range of 7−10 K. However, since the container material for the syntheses, niobium, is itself a superconductor with $T_c = 9.25$ K[8] and could interfere in our conclusions, we also synthesized the compounds in tantalum containers. Tantalum is a superconductor with a critical temperature of 4.47 K.[8] These samples showed the same magnetic behavior as the ones from the niobium containers.

Results and Discussion

The six A_5Pn_4 compounds are isostructural, and the structure is quite simple. It is made of isolated pnictide tetramers and alkali-metal cations (Figure 1). The intertetramer distances are longer than 4.7, 4.4, and 4.0 Å for the bismuthides, antimonides, and the arsenide, respectively, and indicate that there are no direct interactions. The tetramers are exactly planar and with a zigzag shape due to a mirror plane that contains the molecule and an inversion center in the middle, respectively. There are two types of distances: one being the distance between the two middle atoms, Pn1−Pn1, and the other being the two equivalent distances between the end and middle atoms, Pn1−Pn2 (Table 3). For all, the outside distances are shorter than the middle one by about 1% in the arsenide and antimonides and by about 2% in the bismuthides. The distances in all tetramers are shorter than known single-bond distances for the corresponding element. Thus, for the arsenide and the antimonides, they are shorter than the single-bonded helical chains of $(As^-)_\infty$ and $(Sb^-)_\infty$ found in the compounds APn (no such compound is known for bismuth),[9] with distances in the ranges of 2.47−2.50 and 2.83−2.88 Å, respectively, and the single-bonded dimers of Sb_2^{4-} in Cs_4Sb_2 and hexamers of Sb_6^{8-} in Ba_4Sb_6, with distances of 2.923 and 2.86−3.00 Å, respectively.[10] All of them are also shorter than the distances in the corresponding element: 2.52, 2.908, and 3.07 Å for As, Sb, and Bi, respectively.[11] We can also compare them with single- and double-bond distances in molecular compounds of the type $R_2Pn-PnR_2$ and $RPn=PnR$, respectively. Thus, the Bi−Bi distances in $(Me_3Si)_4Bi_2$ and Ph_4Bi_2 are 3.035 and 2.990 Å, respectively,[12] the Sb−Sb distances in Me_4Sb_2, $(Me_3Si)_4Sb_2$, and Ph_4Sb_2 are 2.838, 2.867, and 2.844 Å, respectively,[13] and the As−As distances in Me_4As_2 and $(F_3C)_4As_2$ are 2.429 and 2.463 Å, respectively.[14] The corresponding double-bond distances are 2.8206, 2.833, and 2.8377 Å for bismuth in $(Tbt)_2Bi_2$, $(2,6\text{-}Mes_2H_3C_6)_2Bi_2$, and the naked dianion Bi_2^{2-} in $(K\text{-crypt})_2Bi_2$, respectively,[4,15] 2.642 and 2.656 Å for antimony in $(Tbt)_2Sb_2$ and $(2,6\text{-}Mes_2H_3C_6)_2Sb_2$, respectively,[15b,16] and 2.276 Å for arsenic in $(2,6\text{-}Mes_2H_3C_6)_2As_2$.[15b]

There are three crystallographic positions for the alkali-metal cations in the structure: A1, A2, and A3. While A1 and A2 are surrounded more or less spherically by seven or six pnictogen atoms, respectively, the position A3 has only four such atoms, which are all Pn2 positions (Figure 1), in a square-planar coordination. This allows and perhaps requires the cation A3 to be either above or below the plane of the square to avoid the distances to these atoms being too short. This, for A3, is possible because only cations A1 and A2 are above that plane and they are quite distant from the A3 position.

While the structure of the A_5Pn_4 compounds is fairly simple, the electronic structure and bonding are somewhat more difficult to rationalize. For the charge on the tetramer, there are three possibilities that could be imagined: 6−, 5−, and 4−. The first would correspond to an all in all single-bonded tetramer with the four atoms in sp^3 hybridization, $Pn^{2-}-Pn^{1-}-Pn^{1-}-Pn^{2-}$. This, obviously, is quite impossible since there are only five cations. Furthermore, the tetramer should have been helical and

(8) (a) Poole, C. P., Jr.; Canfield, P. C.; Ramirez, A. P. In *Handbook of Superconductivity*; Poole, C. P., Jr., Ed.; Academic Press: San Diego, CA, 2000. (b) Rose-Innes, A. C.; Rhoderick, E. H. *Introduction to Superconductivity*; Pergamon: Oxford, U.K., 1994.

(9) Hönle, W.; von Schnering, H. G. *Z. Kristallogr*. **1981**, *155*, 307.

(10) (a) Hirschle, C.; Röhr, C. *Z. Anorg. Allg. Chem*. **2000**, *626*, 1992. (b) Eisenmann, B.; Jordan, H.; Schäfer, H. *Z. Naturforsch., B: Chem. Sci*. **1985**, *40*, 1603.

(11) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, U.K., 1984.

(12) (a) Mundt, O.; Becker, G.; Rössler, M.; Witthauer, C. *Z. Anorg. Allg. Chem*. **1983**, *506*, 42. (b) Calderazzo, F.; Poli, R.; Pelizzi, G. *J. Chem. Soc., Dalton Trans*. **1984**, 2365.

(13) (a) Mundt, O.; Riffel, H.; Becker, G.; Simon, A. *Z. Naturforsch., B: Chem. Sci*. **1984**, *39*, 317. (b) Becker, G.; Freudenblum, H.; Witthauer, C. *Z. Anorg. Allg. Chem*. **1982**, *492*, 37. (c) von Deuten, K.; Rehder, D. *Cryst. Struct. Commun*. **1980**, *9*, 167.

(14) (a) Mundt, O.; Riffel, H.; Becker, G.; Simon, A. *Z. Naturforsch., B: Chem. Sci*. **1988**, *43*, 952. (b) Becker, G.; Golla, W.; Grobe, J.; Klinkhammer, K. W.; Le Van, D.; Maulitz, A. H.; Mundt, O.; Oberhammer, H.; Sachs, M. *Inorg. Chem*. **1999**, *38*, 1099.

(15) (a) Tokitoh, N.; Arai, Y.; Okazaki, R.; Nagase, S. *Science* **1997**, *277*, 78. (b) Twamley, B.; Sofield, C. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc*. **1999**, *121*, 3357.

(16) Tokitoh, N.; Arai, Y.; Sasamori, T.; Okazaki, R.; Nagase, S.; Uekusa, H.; Ohashi, Y. *J. Am. Chem. Soc*. **1998**, *120*, 433.

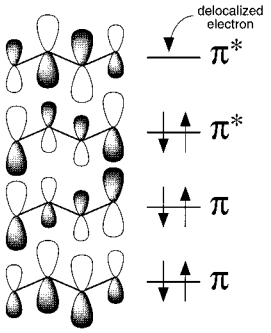

Figure 2. Schematic molecular orbital diagram for π-system of a flat zigzag tetramer. The electron population with six π-electrons corresponds to Pn_4^{4-}. According to our model, one electron per tetramer is delocalized over the structure including, in part, the available antibonding orbital of the tetramer Pn_4^{4-}, i.e., the top π^* (shown).

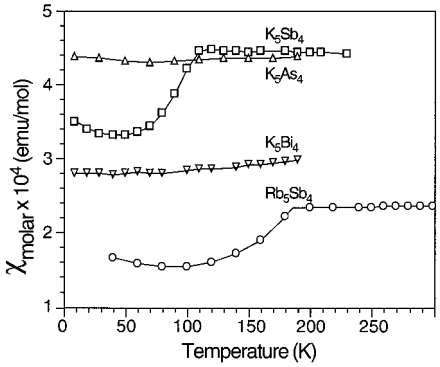

Figure 3. Plots of the magnetic susceptibilities of K_5Sb_4, K_5As_4, K_5Bi_4, and Rb_5Sb_4 as functions of the temperature measured at a field of 3 T. The arsenide and the bismuthide show metallic temperature-independent paramagnetism at all temperatures while the two antimonides are such only above 110 K for K_5Sb_4 and 190 K for Rb_5Sb_4. Below these temperatures they undergo transitions.

not flat for such hybridization, just like the reported hexamer Sb_6^{8-},[10b] and the distances should have been longer than the observed values and closer to the single-bond distances. The second option is a radical of Pn_4^{5-} with seven π-electrons that are, perhaps, delocalized over the tetramer. The third possibility is a tetramer of Pn_4^{4-} with six delocalized π-electrons and an extra electron from the fifth alkali metal (per formula) that would be possibly delocalized over the structure. The latter two options are in agreement with the planar shape of the tetramer. They are also in agreement with the observed Pn−Pn distances that are somewhat shorter than single-bond distances in other compounds. Furthermore, both models would predict a somewhat longer bond in the middle of the tetramer compared to the two outside distances, since the middle two atoms contribute more in the highest occupied molecular orbital (HOMO) than the outside atoms (Figure 2). The radical model would have a net of a half π-bond per tetramer while for Pn_4^{4-} there would be almost a full π-bond delocalized over the species, just like in an isoelectronic butadiene dianion $C_4H_6^{2-}$.

The two models, a radical of Pn_4^{5-} and Pn_4^{4-} with a delocalized electron, would differ in their magnetic properties, since the former should exhibit a temperature-dependent paramagnetism due to the localized spin while the latter should behave like a metal with temperature-independent Pauli-like paramagnetism. Our measurements show that the compounds are of the second type, i.e., their magnetic susceptibilities are positive and temperature independent near room temperature (Figure 3). This is in agreement with two-probe resistivity measurements which show metallic conductivity at room temperature. This puts the compounds in the very rare class of "metallic salts", which can be defined as compounds with isolated, usually complex anions with well-defined charges just like in normal salts, with one or more delocalized electrons that make them metallic. Such compounds are, for example, A_8Tr_{11} (Tr = Ga, In, or Tl), with isolated clusters of Tr_{11}^{7-} and a delocalized electron,[17] and $K_{10}Tl_7$, with isolated clusters of Tl_7^{7-} and three delocalized electrons.[18]

Below 110 and 190 K, the magnetic susceptibilities of the two antimonides K_5Sb_4 and Rb_5Sb_4, respectively, decrease and indicate that they undergo a transition of some kind (Figure 3). The transition temperatures are independent of how the sample is cooled, i.e., with or without magnetic field. The preliminary interpretation is that below these temperatures the delocalized electrons localize, presumably, on the tetramers, making them essentially Pn_4^{5-} and order antiferromagnetically at the same time. However, it is not clear whether the phenomenon is only magnetic transition or if it also involves structural transition. It is also not clear why it occurs only with the antimonides and not with the arsenides and the bismuthides, and more detailed studies of the magnetic properties are currently under way. Some preliminary results for Rb_5Sb_4 from single-crystal X-ray diffraction data collected at 140 K, below the transition temperature of 190 K, seem to indicate doubling of the *b*- and *c*-axes. The structure refinement suggests the ordering of a half of the rubidium cations at the A3 position that was refined statistically disordered as 50% occupied (above) with very short distance to its equivalent. These cations are now ordered alternating between the two possible sites without disorder, essentially causing the doubled axes. It is not clear, however, whether this has any relation to the magnetic transition.

At temperatures close to room temperature, it is clear that electron delocalization takes place over the structure and the delocalized electron would presumably reside for part of the time on the tetramer, bringing the value of the formal charge of the tetramer to anywhere between −4 and −5, i.e., $Pn_4^{(4+\delta)-}$. The only available molecular orbital for this additional charge δ is the most antibonding π^* (Figure 2). This will lower the overall bond order of the molecule below one π-bond per tetramer, or in other words, the average total bond order will be less than 1.33 per bond. The result is bond elongation compared to one full π-bond per tetramer and explains why the observed Pn−Pn distances are only slightly shorter than the corresponding single-bond distances. The bond order n can be estimated from Pauling's formula: $\log(n) = (d_1 - d_n)/0.6$ where d_1 and d_n are the single-bond and the observed distances, respectively.[19] Using the values $d_1 = 2.489$ and 2.841 Å for As and for Sb, respectively, from the helical chains in KAs and KSb[9] and $d_1 = 3.07$ Å for Bi in elemental bismuth (since there is no solid-state compound for negatively charged bismuth with a single bond),[11] we obtain $n = 1.18$ and 1.28 for the two different bonds of the tetramer in K_5As_4, $n = 1.09$ and 1.22 for K_5Sb_4, and $n = 1.09$ and 1.32 for K_5Bi_4. The same phenomenon is observed in the compounds A_3Bi_2 (A = K, Rb, Cs) with isolated dimers of Bi_2^{2-} where, similarly, an extra electron is delocalized over the structure, resides partially on a π^*-orbital of the dimer, and leads to a bond order lower than 2.[3] This is also manifested by distances that are longer than that expected

(17) (a) Sevov, S. C.; Corbett, J. D. *Inorg. Chem.* **1991**, *30*, 4875. (b) Blase, W.; Cordier, G.; Müller, V.; Häussermann, U.; Nesper, R.; Somer, M. *Z. Naturforsch., B: Chem. Sci.* **1993**, *48*, 754. (c) Dong, Z. C.; Corbett, J. D. *J. Clust. Sci.* **1995**, *6*, 187.
(18) Kaskel, S.; Corbett, J. D. *Inorg. Chem.* **2000**, *39*, 778.
(19) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960; p 239.

for a Bi−Bi double bond (observed distances of ca. 2.976 Å and bond order of ca. 1.43).[3]

The angles in the tetramers are smaller than the typical 120° for sp^2 hybridization: 109.85(6), 107.32(7), and 106.30(8)° in K_5As_4, K_5Sb_4, and K_5Bi_4, respectively. This indicates that the s- and p-orbitals for these heavier homologues of group 15 are not significantly mixed, as might be expected. Furthermore, there is a lone pair of electrons at Pn1 and its stronger repulsion will also favor a smaller angle.

Magnetic measurements of the potassium and rubidium bismuthides at low temperatures and low fields showed sharp drops in magnetic susceptibilities reminiscent of superconducting transitions. Among the enormous number of known solid-state compounds with different stoichiometries, structures, properties, etc., only a meager few, about 300, exhibit that property below temperatures higher than the boiling point of helium (4.2 K).[7a] The finding of a new superconducting compound, therefore, is an important discovery and even more so when it has a novel structure. The susceptibilities of the ZFC and FC samples clearly show hystereses that are typical for type-II superconductors (Figure 4a). The onset temperatures are about 9.5 and 10 K for K_5Bi_4 and Rb_5Bi_4, respectively. It should be explained here that the magnetization shown in Figure 4a does not become negative due to the presence of a relatively large fraction of KBi_2 in this particular sample. This latter compound is a Laves phase of the $MgCu_2$ type and is also superconducting but below 3.5 K,[7] at which temperature the whole multiphase product becomes superconducting and the magnetization becomes negative. In addition to these 5:4 phase superconducting compounds, there are also the recently reported A_3Bi_2 compounds with transition temperatures of ca. 7.5 K for the potassium salt.[3] Their magnetizations above T_c are also positive and temperature independent and indicate metallic compounds. As mentioned above, these compounds contain isolated Bi_2^{2-} dimers and an extra delocalized electron.[3] Figure 4b shows the temperature dependence of the magnetization of a sample of K_3Bi_2 containing a small amount of K_5Bi_4 as well. The onset temperature for the major phase is ca. 7.5 K, and the relatively large hysteresis between the two types of cooling indicates a relatively low upper critical field H_{c2}. Measurements of the dependence of the magnetization of K_3Bi_2 on the applied magnetic field at temperatures below $T_c = 7.5$ K, i.e., in superconducting state, showed close resemblance to the curve expected for type-II superconductors.[7b] From these measurements and from measurements of T_c at different fields, we estimate the two critical fields H_{c1} and H_{c2} to be approximately 100 and 1100 G, respectively. The curves of magnetization vs field for K_5Bi_4 were quite "smeared", and it was impossible to estimate the critical fields from them. Nevertheless, the T_c dependence of the field gave a value of ca. 1300 G for H_{c2}. Unfortunately, due to the extremely high instability of the compounds toward moisture and oxygen, measurements of the electrical conductivity were not carried out.

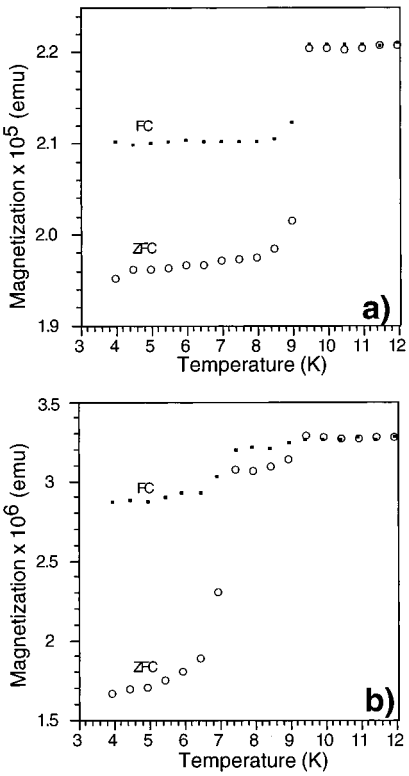

Figure 4. Plots of the magnetization of field-cooled (FC) and zero-field-cooled (ZFC) samples of (a) K_5Bi_4 and (b) K_3Bi_2 measured at a field of 100 Oe. They reveal superconducting transitions at about 9.5 and 7.5 K for the two compounds, respectively. The hystereses clearly indicated type-II superconductors. The small step at around 9.5 K in (b) is due to some amount of K_5Bi_4 mixed in the K_3Bi_2 sample. Both compounds were also contaminated with some amounts of KBi_2, which is superconducting below 3.5 K.

All potassium compounds K_5Pn_4 as well as K_3Bi_2 dissolve readily in ethylenediamine mixed with 2,2,2-crypt. The solution of K_5Bi_4 behaves exactly like the solution of K_3Bi_2; i.e., when layered with toluene it provides crystals of $[K\text{-crypt}]_2Bi_2$ with the double-bonded molecule $[Bi{=}Bi]^{2-}$ [4] and when reacted with (mesitylene)(Cr or Mo)$(CO)_3$ it provides the mixed-atom cluster $[Bi_3M_2(CO)_6]^{3-}$.[5]

Acknowledgment. We thank the Petroleum Research Fund, administered by the ACS, for the financial support of this research.

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

IC0104499