KSb₂, a New Structure Composed of Ribbons of Edge-Shared Six-Membered Sb Rings

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Introduction

There are a number of binary compounds which can be described as valence compounds and whose structures can be rationalized using the Zintl−Klemm rule, and are therefore considered to be Zintl compounds. Although some of these binary compounds are made up of anionic partial structures that are isoelectronic and isostructural with elemental structures, there are a large number of compounds with entirely new anionic structures.[1-3] Considering the large number of binary compounds that exist whose structures are known, it is surprising that there are new structures still waiting to be discovered. Serendipity sometimes is the key,[4] and herein we describe the synthesis, structure, and electronic characterization of the Zintl compound KSb₂.

There are several binary compounds known in the potassium−antimony system.[5] The phase diagram indicates the presence of four compounds, K₃Sb, K₅Sb₄, KSb, and KSb₂. The structures of the first three compounds are known. K₃Sb[6,7] crystallizes in the Na₃As structure type with isolated Sb, K₅Sb₄[8] forms zigzag chains of four Sb atoms and KSb[9,10] forms infinite helical Sb chains along the *b*-axis. During our attempts to make new ternary intermetallic compounds in the K−Sb system with a transition metal we obtained single crystals of the KSb₂ phase.

Experimental Section

Synthesis. Materials utilized were K (Mallinckrodt), which was trimmed of oxidation products, Mn (J. Matthey (99.99%)) flakes, cleaned with a solution of 15% HNO₃, 85% methanol, then rinsed with acetone and ground into powder, and Sb shot (J. Matthey (99.9999%)). The elements were combined in the ratio 1:1:1 (K:Mn:Sb) in a nitrogen-filled drybox, placed into a niobium tube, and sealed with an argon arc welder. The niobium tube was then sealed in a fused silica ampule with an argon pressure of 60 Torr. The reaction mixture was heated (60 °C/h) to 1050 °C for 3 h, cooled (60 °C/h) to 850 °C, and annealed at this temperature for 1 week. Then the furnace was turned off and the sample allowed to cool in the furnace. Black crystals were obtained in addition to the known compound, KMnSb.[11] The products were

handled in a drybox. Crystals of KSb₂ were separated and transferred to Paratone-N oil for X-ray determination.

Quantitative yields of KSb₂ can be obtained by mixing stochiometric amounts of the elements and performing the reaction in an Al₂O₃ crucible sealed under argon in a fused silica ampule. The reaction (heating at 450 °C for 10 h and cooling (50 °C/h) to room temperature) produced polycrystalline material along with small cystals of KSb₂. The black, metallic looking crystals of KSb₂ decompose quickly when exposed to air.

Crystallography. A black crystal of dimensions 0.40 × 0.10 × 0.12 mm was used for the single crystal X-ray diffraction measurements. Data were collected ($2\theta_{max} = 108°$; $-18 \leq h \leq 18, 0 \leq k \leq 5, 0 \leq l \leq 9$) on a four-circle diffractometer (Siemens P4 rotating anode, 45kV, 200mA) at 120K with Ni-filtered Cu Kα radiation. The lattice parameters were refined using 24 reflections between angles of 5 and 35 in 2θ. A total of 579 refections were collected (579 independent, 521 ($F > 4.0\sigma(F)$) observed) Crystallographic parameters are summarized in Table 1. The data were corrected for Lorentz and polarization effects. Crystallographic programs were those of SHELX-TL PLUS, Version 4.0, installed on a MicroVAX computer.[12] Scattering factors and corrections for anomalous dispersion were those supplied with SHELXTL.

There were three possible space groups *C2*, *Cm* and *C2/m*. Intensity statistics indicated a centrosymmetric structure. The choice of *C2/m* was supported by subsequent calculations. The structure was solved by direct methods and the refinement proceeded without any complications. An empirical absorption correction (XABS2)[13] was applied after the refinement converged with isotropic *U*'s. Atomic coordinates and isotropic *U*'s are given in Table 2. Tables of data collection and refinement parameters, anisotropic *U*'s, and bond lengths and angles are provided as Supporting Information.

Powder X-ray Diffraction. Powder diffraction patterns were obtained on powdered samples mounted between two pieces of commercially available transparent tape with approximately 5% NIST Si (by volume) as an internal standard. An Enraf-Nonius Guinier camera utilizing Cu Kα₁ radiation was employed. All the lines in the powder diffraction pattern could be indexed according to the structure of KSb₂. Room temperature lattice parameters for KSb₂ are $a = 14.176$-(2) Å, $b = 4.2419(5)$ Å, $c = 7.0928(9)$ Å, and $\beta = 95.10(1)°$. Calculated versus experimental *d* spacings and intensities are provided as supplemental material. The powder diffraction pattern of KSb₂ reported by Dorn et al.[5] has a few additional lines, but is consistent with the calculated pattern for the structure reported herein.

Resistivity. Temperature dependent resistivity was obtained for a pressed pellet of KSb₂. KSb₂ was ground into a powder and subsequently pressed into a 6.4 mm diameter by 2 mm thick pellet in a drybox. The pellet was then placed under four stainless steel probes with indium between each stainless steel probe and the pellet for better contact. This setup was then sealed under nitrogen and transferred to the resistivity apparatus. A current of 1 mA (Keithley Model 224 current source) was applied, and the voltage was measured with a Keithley Model 182 nanovoltmeter for $15 \text{ K} \leq T \leq 300 \text{ K}$ at 5 K intervals.[14] The sample exhibited ohmic behavior.

Results and Discussion

Surprisingly, the characterization of the APn₂ (A = alkali metal Pn = pnictogen) binary compounds is rather incomplete. The ABi₂ compounds (A = K, Rb, Cs)[15-17] represent the most

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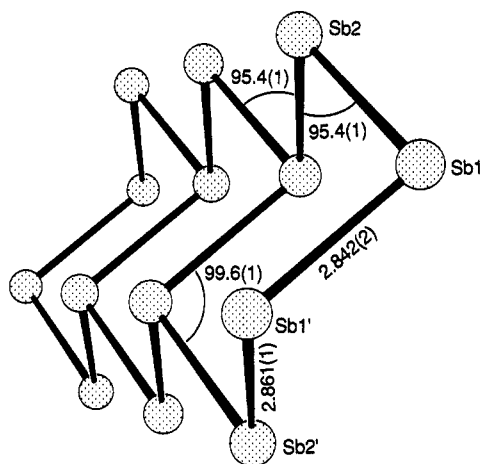**Table 1.** Selected Data Collection and Refinement Parameters
for KSb₂

chem formula	KSb₂	fw	282.6
a (Å)	14.055(5)	space group	$C2/m$
b (Å)	4.233(1)	T (°C)	−153
c (Å)	7.053(2)	λ(Cu Kα) Å	1.5418
β (deg)	95.02(3)	ρ_{calc} (g cm⁻³)	4.49
		μ(Cu Kα) (cm⁻¹)	1094.7
V (Å³⁾	418.0(2)	R (%)	4.75
Z	4	$R_w{}^a$ (%)	5.17

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_w = \Sigma||F_o| - |F_c||w^{1/2}/\Sigma|F_ow^{1/2}|$.

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic
Displacement Coefficients (Å² × 10³)

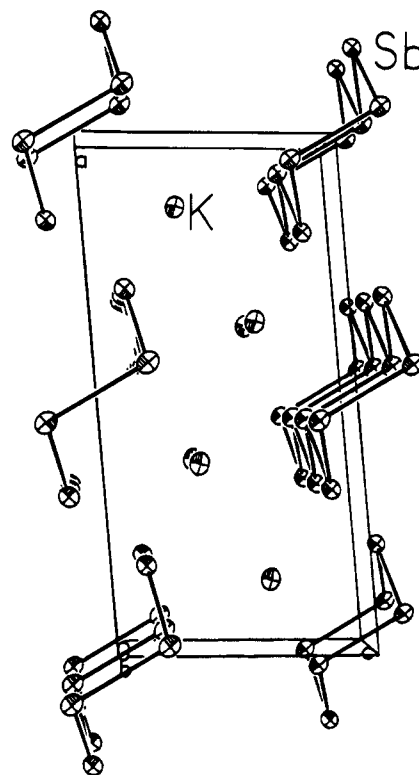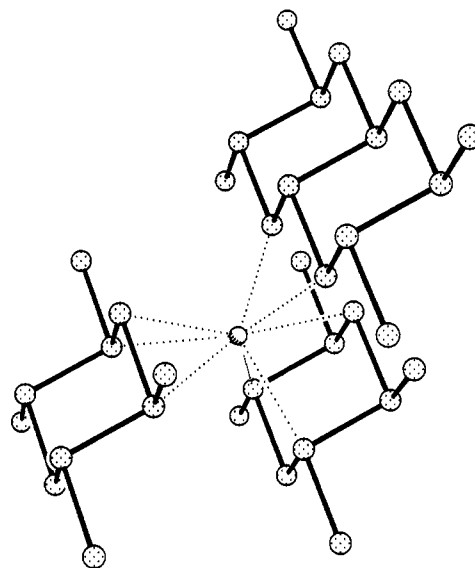| atom	x	y	z	U(eq)^a
Sb(1)	514(1)	0	1828(1)	11(1)
Sb(2)	1835(1)	5000	1303(1)	10(1)
K	1341(3)	5000	6287(4)	15(1)

^{a} Equivalent isotropic U defined as one third of the trace of the
orthogonalized $\mathbf{U}_{ij}$ tensor.

Figure 1. Connectivity of the Sb₂⁻ anionic framework with bond
lengths.

Figure 2. View down the b-axis of the unit cell of KSb₂. The K⁺
atoms are located in a layer parallel to the $_\infty^1$Sb₂⁻ ribbons. Thermal
ellipsoids are shown at 90%.

Figure 3. View showing the coordination of the K atom with respect
to the $_\infty^1$Sb₂⁻ ribbons.

complete series of compounds whose structures are known. They
were first synthesized in 1932 by Zintl and were shown to
crystallize in the MgCu₂ structure-type from powder X-ray
diffraction. Only the compound KAs₂[18] has been reported of
the AAs₂ compounds and its structure has not been determined.
Both RbSb₂ and CsSb₂ are also reported, but their structures
were also not determined.[5]

KSb₂ represents a new structure type that shows a unique
polyanionic framework. Figure 1 shows the connectivity of the
(Sb₂)⁻ anionic framework along with bond lengths and angles.
The structure is built up by anionic ribbons which are three
dimensionally connected by the K cation. There are two
different Sb atoms, Sb(1) which has three Sb neighbors and
Sb(2) which has only two. The Sb atoms form six-membered
rings which are connected to the next ring via a common edge
to form an infinite ribbon. The Sb(1)−Sb(2) bond length is
2.861(1) Å, slightly longer than the Sb(1)−Sb(1) distance of
2.842(1) Å. This slight elongation is consistent with the higher
coordination number observed for Sb(1). Typical Sb−Sb bond
lengths are 2.790−2.815 Å in K₅Sb₄,[8] 2.829−2.852 Å in KSb,[10]
and 2.908 Å in the element.[19]

Figure 2 shows the $_\infty^1$Sb₂⁻ ribbons in the framework of the
unit cell. The ribbons are oriented along the a-axis, with

stacking along the c-axis. The ribbons are stacked so that the
Sb with two neighbors fit in the gap of the next ribbon.

The K⁺ atoms are located in a layer parallel to the ribbon's
(110) plane. Figure 3 shows the local coordination around K.
It has short bonds of 3.545−3.694 Å which connect two Sb
ribbons of different layers and form a distorted octahedron
around the K. There are two additional longer bonds of 3.884
Å that are shown in Figure 3. There are four K atoms in a
plane with one Sb above and another one below this plane. The
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These six-membered rings can also be seen in the isoelectronic unit $^1_\infty Te_2^+$ found in the tellurium subhalides[20,21] and $^1_\infty X_2^{3-}$ (X = Si, Ge) found in Sr_3Ge_4 and $Ca_{0.5}Sr_{2.5}Si_2$.[2] The difference is in the conformation of the rings. In the case of KSb_2, the Sb six-membered ring is in the chair conformation, whereas the isoelectronic Te six-membered ring is in a boat conformation.[20,21] Sr_3Ge_4 which is isotypic to $Ca_{0.5}Sr_{2.5}Si_4$, forms infinite ribbons of planar hexagons.[2] Considering the wide variety of anionic frameworks that Zintl compounds show[1-3,22-25] it is surprising that this particular conformation is unique. The chair conformation of the $^1_\infty Sb_2^-$ ribbons can be compared with the Si_2^{2-} in, for example, $CaSi_2$[26] but instead of one dimensional ribbons the silicon forms a two dimensional plane similar to arsenic.[19] It is interesting to note that (crypt-K^+)$_2Sb_4^{2-}$[27] has the same anion, $2Sb_2^- = Sb_4^{2-}$, but forms a square plane. There are several phosphorus compounds that are composed of six-membered rings connected in different fashions.[3] The anionic framework in LiP_5 shows the most similarity to that of KSb_2; P forms infinite ribbons of P in chair conformation, which are connected three dimensionally with an extra P.[28]

Temperature dependent resistivity shows activated behavior indicating that this compound is a semiconductor. The ln ρ versus $1/T$ shows typical saturation effects at low temperatures.[29] The data can be fitted over the temperature range 200–300 K to the equation ln $\rho = E_a/k_BT + C$ to give $E_a = 0.011(4)$ eV and $C = 1.89(1)$. The room temperature resistance of the pressed pellet is 84.5(1) Ω cm.

The bond lengths are consistent with the interpretation of covalent bonding within the anionic framework. Regarding the generalized $(8 - N)$ rule, the Sb atoms have the formal charge of 0 when bonded to three neighbors, similar to the element, and they have the formal charge of -1 when they have two neighbors, similar to the elements to the right. Therefore this compound belongs to the Zintl phases and to the large class of valence compounds.

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