KSb_2, a New Structure Composed of Ribbons of Edge-Shared Six-Membered Sb Rings

Anette Rehr, Francisco Guerra, Sean Parkin,† Håkon Hope, and Susan M. Kauzlarich*

Department of Chemistry, University of California, Davis, California 95616

Received June 7, 1995

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 KSb_2.

There are several binary compounds known in the potassium−antimony system.[5] The phase diagram indicates the presence of four compounds, K_3Sb, K_5Sb_4, KSb, and KSb_2. The structures of the first three compounds are known. K_3Sb[6,7] crystallizes in the Na_3As structure type with isolated Sb, K_5Sb_4[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 KSb_2 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% HNO_3, 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 KSb_2 were separated and transferred to Paratone-N oil for X-ray determination.

Quantitative yields of KSb_2 can be obtained by mixing stochiometric amounts of the elements and performing the reaction in an Al_2O_3 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 KSb_2. The black, metallic looking crystals of KSb_2 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 ($2\theta_{max} = 108°$; $-18 \le h \le 18$, $0 \le k \le 5$, $0 \le l \le 9$) 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 SHELXTL 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 *C*2, *Cm* and *C*2/*m*. Intensity statistics indicated a centrosymmetric structure. The choice of *C*2/*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 $K\alpha_1$ radiation was employed. All the lines in the powder diffraction pattern could be indexed according to the structure of KSb_2. Room temperature lattice parameters for KSb_2 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 KSb_2 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 KSb_2. KSb_2 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 K $\le T \le$ 300 K at 5 K intervals.[14] The sample exhibited ohmic behavior.

Results and Discussion

Surprisingly, the characterization of the APn_2 (A = alkali metal Pn = pnictogen) binary compounds is rather incomplete. The ABi_2 compounds (A = K, Rb, Cs)[15−17] represent the most

† Current address: L-452, BBRP, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550.

(1) von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 33.
(2) Schäfer, H.; Eisenmann, B.; Müller, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 694.
(3) von Schnering, H.-G.; Hönle, W. *Chem. Rev.* **1988**, *88*, 243.
(4) Corbett, J. D. *Pure Appl. Chem.* **1984**, *56*, 1527.
(5) Dorn, F. W.; Klemm, W. *Z. Anorg. Allg. Chem.* **1961**, *309*, 189−203.
(6) Sommer, A. H.; McCarroll, W. H. *J. Appl. Phys., N.Y.* **1966**, *37*, 174−179.
(7) Brauer, G.; Zintl, E. *Z. Phys. Chem.* **1937**, *37B*, 323−352.
(8) Somer, M.; Hartweg, M.; Peters, K.; von Schnering, H. G. *Z. Kristallogr.* **1991**, *195*, 103−104.
(9) Busmann, E.; Lohmeyer, S. *Z. Anorg. Allg. Chem.* **1961**, *312*, 53−59.
(10) Hönle, W.; von Schnering, H. G. *Z. Kristallogr.* **1981**, *155*, 307−314.
(11) Schuster, H.-U.; Achenbach, G. *Z. Naturforsch.* **1978**, *33B*, 113.
(12) Sheldrick, G. M. SHELXTL PLUS. Program for crystal structure determination. Madison, WI, 1991.
(13) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53−56.
(14) Sunstrom, J. E., IV. DCRES: A Quickbasic program for temperature dependent resistivity data collection and analysis. 1991, University of California, Davis, 1991.
(15) Zintl, E.; Harder, A. *Z. Phys. Chem.* **1932**, *16B*, 206−212.
(16) Gunteman, G.; Klemm, W. *Z. Anorg. Allg. Chem.* **1961**, *309*, 181−188.
(17) Grutsmann, G.; Dorn, F. W.; Klemm, W. *Z. Anorg. Allg. Chem.* **1961**, *309*, 210−225.

0020-1669/95/1334-6218$09.00/0

Table 1. Selected Data Collection and Refinement Parameters for KSb_2

chem formula	KSb_2	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 (Å^3)	418.0(2)	R (%)	4.75
Z	4	R_w[a] (%)	5.17

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

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

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 U_{ij} tensor.

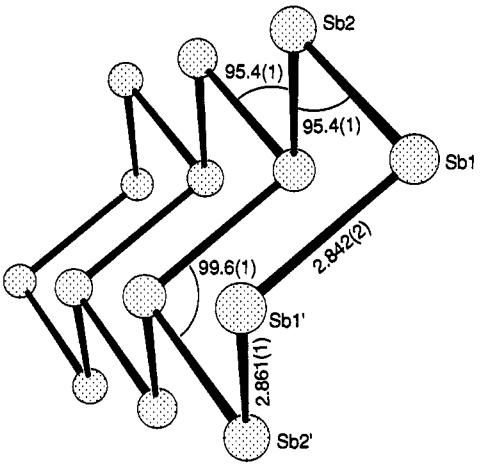

Figure 1. Connectivity of the Sb_2^- anionic framework with bond lengths.

complete series of compounds whose structures are known. They were first synthesized in 1932 by Zintl and were shown to crystallize in the $MgCu_2$ structure-type from powder X-ray diffraction. Only the compound KAs_2[18] has been reported of the AAs_2 compounds and its structure has not been determined. Both $RbSb_2$ and $CsSb_2$ are also reported, but their structures were also not determined.[5]

KSb_2 represents a new structure type that shows a unique polyanionic framework. Figure 1 shows the connectivity of the $(Sb_2)^-$ 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 K_5Sb_4,[8] 2.829−2.852 Å in KSb,[10] and 2.908 Å in the element.[19]

Figure 2 shows the $^1_\infty Sb_2^-$ ribbons in the framework of the unit cell. The ribbons are oriented along the a-axis, with

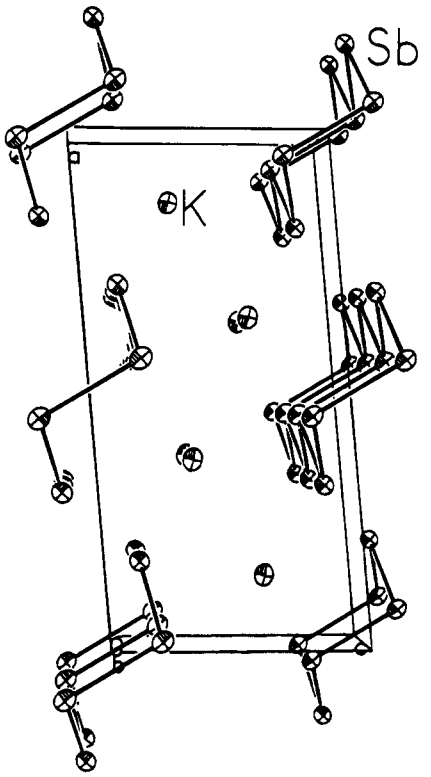

Figure 2. View down the b-axis of the unit cell of KSb_2. The K^+ atoms are located in a layer parallel to the $^1_\infty Sb_2^-$ ribbons. Thermal ellipsoids are shown at 90%.

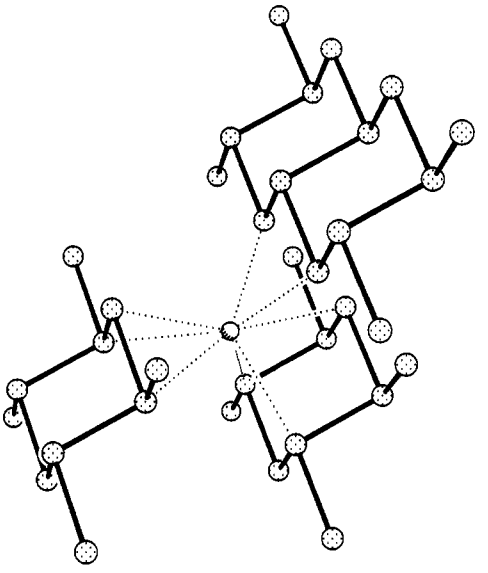

Figure 3. View showing the coordination of the K atom with respect to the $^1_\infty Sb_2^-$ ribbons.

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 octahedron shares trans-edges of K with the next octahedron.

(18) Dorn, F. W.; Klemm, W.; Lohmeyer, S. Z. *Anorg. Allg. Chem.* **1961**, *309*, 204−209.

(19) Wells, A. F. *Structural Inorganic Chemistry;* 5th ed.; Oxford University Press: New York, 1984; pp 1277−1280.

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 $(crypt\text{-}K^+)_2Sb_4^{2-}$[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.

Acknowledgment. We gratefully acknowledge M. M. Olmstead and B. C. Noll for useful discussions, the National Science Foundation (Grants DMR-8913831, -9201041) for financial support and the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship for A.R.

Supporting Information Available: Tables of data collection and refinement parameters, anisotropic thermal parameters, bond lengths and angles, and powder diffraction data (4 pages). Ordering information is given on any current masthead page.

IC9507068

(20) Kniep, R.; Mootz, D.; Rabenau, A. *Angew. Chem.* **1973**, *85*, 504.
(21) Kniep, R.; Mootz, D.; Rabenau, A. *Z. Anorg. Allg. Chem.* **1976**, *422*, 17−38.
(22) Schäfer, H.; Eisenmann, B. *Rev. Inorg. Chem.* **1981**, *3*, 29.
(23) Schäfer, H. *Annu. Rev. Mater. Sci.* **1985**, *15*, 1.
(24) Nesper, R. *Prog. Solid State Chem.* **1990**, *20*, 1.
(25) Corbett, J. D. *Chem. Rev.* **1985**, *85*, 383.
(26) Janzon, K. H.; H., S.; Weiss, A. *Z. Anorg. Allg. Chem.* **1970**, *372*, 87−99.
(27) Critchlow, S. C.; Corbett, J. D. *Inorg. Chem.* **1984**, *23*, 770−774.
(28) Hoffmann, R. P.; Caulton, K. G. *Inorg. Chem.* **1975**, *16*, 1997.
(29) Cox, P. A. *The Electronic Structure and Chemistry of Solids*; Oxford University Press: Oxford, England, 1987; p 202.