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A Zintl Phase with a Layered Network Structure, KSi_3As_3

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The title compound is obtained in high yield from a two-step reaction of K with Si in sealed tantalum and then of that product with As in silica at 800–900 °C. Ion exchange with NaI at 500 °C gives the sodium derivative. The structure of the purple KSi_3A_3 crystals has been established by X-ray diffraction means at room temperature (orthorhombic, space group *Pbam*, $Z = 4$, $a = 10.010$ (4) Å, $b = 19.139$ (8) Å, $c = 3.664$ (1) Å, $R = 0.044$ for 674 reflections, $2\theta < 55°$). The ${}^2_\infty[Si_3As_3]^-$ anion layers may be generated by Si–Si bonding between puckered $Si_3As_3(As)$ rings to form chains followed by side-by-side condensation of these to sheets. The structure may be derived from the layered structure of SiAs in a concerted way through reductive ring opening and Si–Si bond formation. Comparisons are also made with more reduced Si–As anion chains and clusters and with the closely related Li_3NaSi_6. K_2SiAs_2 has also been synthesized and shown to be isostructural with K_2SiP_2.

Introduction

Binary compounds between silicon, germanium, etc. (A) and phosphorus, arsenic, etc. (B) have been known for a long time.[2-4] The most common stoichiometries are AB and AB_2, which at ambient temperature and pressure often exhibit layered structures. In the former GaTe type, A is bonded to three B atoms and one A atom in a structure of condensed tetrahedra, while in the latter, typified by $GeAs_2$, A is bound to four B atoms that share edges to form layers that bear some resemblance to those in the former. These are all valence of Zintl[5,6] phases and semiconductors at room temperature.[7]

There are only a few known ternary phases $M_xA_yB_z$ for these A and B elements in which M is an alkali metal.[8-10] The structure of the $A_yB_z^{x-}$ anion in such ternary phases is expected to be different from that of the neutral analogue A_yB_z. For instance, the layer structure of SiP_2 ($GeAs_2$ type) is broken down to chains in the formation of K_2SiP_2.[9] It is easy to rationalize this in terms of the reduction that accompanies the formation of SiP_2^{2-}. The latter is isoelectronic with SiS_2, and thus K_2SiP_2 has a structure similar to that of SiS_2. Likewise, the layered anions in the isostructural KSnAs and KSnSb phases are isoelectronic with $CaSi_2$ and have a structure like that of $CaSi_2$ but with ordered tin and arsenic or antimony atoms.[10] The anion layers in the $CaSi_2$ structure can in turn be related to the puckered neutral layers found in the isoelectronic element arsenic etc.

Recently, a new composition and structure type has been discovered in our laboratory for MSi_3As_3 (M = K, Na). The relatively low proportion of the alkali metal also allows a clear relationship to be discerned between the $Si_3As_3^-$ structure and that of the binary phase SiAs (GaTe type).[2]

Experimental Section

Synthesis. Materials utilized were purified potassium (J. T. Baker Chem. Co.), which was first trimmed of oxidation products in the drybox, arsenic lumps (99.99% total, Alfa Products) and zone-refined, electronic grade silicon.

The new KSi_3As_3 was first encountered after a reaction of the three elements in a 1:1:1 ratio. This was carried out in a fused silica ampule that had been sealed under vacuum and further jacketed in a second evacuated silica jacket in order to protect the products if container attack led to cracking when the reaction was cooled. The loading of the reactants and the examination of the products were carried out in a glovebox flushed with nitrogen and kept at a moisture level below 5 ppm. Purple, needle-shpaed crystals were found on the inner surface of the container after the reaction had been run in a vertical tube furnace at around 800 °C for 5 days. X-ray emission spectroscopy confirmed the presence of all three elements in the product.

Since potassium attacks a silica container and arsenic attacks the alternative container tantalum, a two-step synthetic process was developed to avoid such side reactions. After the correct stoichiometry of the needles had been determined from a solution of the crystal structure, KSi[11] or "KSi_3", an intimate fused mixture of Si and KSi, were first prepared in high purity by reaction of elemental potassium and silicon in a sealed tantalum container at 800 °C. Stoichiometric amounts of As were then reacted with KSi plus Si or "KSi_3" in sealed fused silica ampules at 910–950 °C for 4–5 days according to eq 1. This approach

$$KSi + 2Si + 3As \rightarrow KSi_3As_3 \qquad (1)$$

greatly reduced the attack of potassium and provided a high yield of the evidently single-phase product, >95% judging from Guinier powder diffraction. Large needle crystals about 8 mm long were found at the top of the ampules where the temperature had been lower. It is presumed that a chemical transport reaction was responsible for this crystal growth, but the process has not been studied further. Iodine does not effect transport in this system, evidently because the stability of the alternate KI is too high.

Attempts at the synthesis of KGe_3As_3 and $NaSi_3As_3$ by the above method in silica and of KGe_3As_3 and KSi_3P_3 by the two-step process were without success although a few small needle crystals were seen in the first of these. However, the phase $NaSi_3As_3$ could be obtained by a cation-exchange method. Equimolar amounts of KSi_3As_3 and NaI were ground together, pressed into a pellet, sealed in a silica tube under vacuum, and heated in a horizontal tube furnace at ~500 °C for 1 week. The end of the tube not containing the pellet was slightly exposed at the end of the furnace, either from the beginning or after several days. Crystals of KI were found at the cold end of the tube (as identified by X-ray lattice constant and qualitative tests), while pure $NaSi_3As_3$ was left in the hot end. Cell constants for $NaSi_3As_3$, $a = 10.002$ (4), $b = 18.54$ (3), and $c = 3.648$ (1) Å, were determined by least-squares refinement of 2θ values for the clearest 10 of the 17 rather broad lines observed in the Guinier powder pattern.

Similar exchange reactions with RbI and CsI were also tried but without success. Exchange reactions at 500 °C employing equimolar amounts of LiI and KSi_3As_3 either as a pressed pellet in SiO_2 under a temperature gradient or as the mixed powders in sealed Ta isothermally likewise produced pure KI judging from the lattice constant. However, the presumed $LiSi_3As_3$ product has a different and unknown crystal structure; the pattern could also result from a mixture.

The potassium phase is not oxidized by benzophenone in THF at ~86 °C, contrary to the observations for Li_7Ge_{12},[12] presumably because of either a low potassium mobility or an insufficient reducing power. The lithium product gives only a faint yellow color under the same conditions

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[1] This research was supported by the Office of Basic Energy Sciences, Materials Sciences Division. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

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Table I. Diffraction and Refinement Data of KSi_3As_3

space group	*Pbam* (No. 55)	μ(Mo Kα), cm^{-1}	112.9
Z	4	transm coeff range	0.87–1.00
cell dimens,[a] Å		reflcn data	
a	10.010 (4)	checked	2405
b	19.139 (8)	obsd ($>3\sigma(I)$)	1551
c	3.664 (1)	indep reflcns	674
cryst size, mm	0.05 × 0.05 × 0.8	R(av)	0.038
octants measd	h,k,l; $-h,-k,l$	struct solution	
scan type	ω	R^b	0.044
2θ(max), deg	55	R_w	0.050

[a] The cell dimensions calculated from 21 lines of the Guinier powder pattern, Cu Kα_1, λ = 1.54056 Å. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Table II. Positional and Isotropic Thermal Parameters for KSi_3As_3[a]

atom	x	y	z	B,[b] Å^2
As(1)	0.4000 (1)	0.19698 (6)	0.0	1.38 (3)
As(2)	0.7191 (1)	0.04102 (5)	0.0	1.17 (3)
As(3)	0.5861 (1)	0.38496 (6)	0.5	1.23 (3)
K[c]	0.1962 (3)	0.3048 (2)	0.5	2.63 (8)
Si(1)	0.3251 (3)	0.1320 (1)	0.5	1.24 (7)
Si(2)	0.1126 (3)	0.5147 (1)	0.5	1.00 (7)
Si(3)	0.4072 (3)	0.5365 (1)	0.0	1.02 (7)

[a] Space group *Pbam*; Z = 4; all atoms in 4h or 4g positions. [b] Average of anisotropic values. [c] Refined occupancy = 0.98 (1).

so the latter explanation is more likely. KSi_3As_3 is not very sensitive to moist air but reacts with water or dilute HCl with vigorous evolution of hydrogen and the formation of a black amorphous product. The lithium product is quite air-sensitive.

The phase K_2SiAs_2 was also obtained from the appropriate reaction of the elements in silica under Ar at 750 °C. The product crystals were shown by means of oscillation, Weissenberg, and Guinier film studies to have the *Ibam* space group of and to be isostructural with K_2SiP_2:[9] a = 13.22, b = 7.02, and c = 6.33 Å ($\sigma \sim$ 0.02 Å).

Structural Studies. A suitable needle crystal (about 0.02 × 0.02 × 0.8 mm) of what turned out to be KSi_3As_3 was mounted and sealed in a 0.2-mm diameter thin-walled capillary. Oscillation and zero- and first-level Weissenberg photographs showed that the cell was orthorhombic with $a \cong 10.1$, $b \cong 19.1$, and $c \cong 3.65$ Å and that the diffraction data exhibited the following nonextinction conditions: $h0l$, $h = 2n$; $0kl$, $k = 2n$; $h00$, $h = 2n$; $0k0$, $k = 2n$. Only two space groups, *Pbam* and *Pba*2, satisfy these, and the structural refinement proved that the centric *Pbam* was correct.

Diffraction data were collected from the same crystal at room temperature and to 2θ = 55° with the aid of graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) and a DATEX four-circle diffractometer. No decay of the standard reflections was observed.

The positions of the three heavier arsenic atoms were first determined with the aid of a Patterson map, and those of the other atoms were then deduced from Fourier F-synthesis maps. It turned out that all atoms occupy the 4(g) (x, y, 0) or 4(h) (x, y, $^1/_2$) positions of m symmetry. The data were corrected for absorption by the ψ-scan method together with the program ABSN. This program and ALLS for structure factor calculations and least-squares refinements, FOUR for Fourier syntheses, and ORTEP for drawings have been referenced before.[13] Scattering factors included the real and imaginary part of anomalous dispersion.[14] A difference map computed after the final cycle showed maximum residual densities between +1.9 and +1.5 e/Å^3. These were all located 0.8–1.4 Å from the As(1), As(2), As(3), or Si(1) positions, generally in outward directions from the layers as might be produced by a small amount of cation defects. Details of crystal data collection and refinement parameters are given in Table I. Lattice parameters calculated from Guinier powder pattern data with Si as an internal standard[13] were used for distance calculations.

Results and Discussion

The positional parameters for KSi_3As_3 are listed in Table II and some important distances and angles are given in Table III. The structure factor data and anisotropic thermal parameters are available as supplementary material.

Table III. Distances (Å) and Angles (deg) in KSi_3As_3

	dist		angle
As(1)–2Si(1)	2.337 (2)	Si(1)–As(1)–Si(1)	103.2 (1)
As(1)–2K	3.431 (3)		
As(1)–2K	3.486 (3)		
As(2)–2Si(2)	2.372 (2)	Si(2)–As(2)–Si(2)	101.2 (1)
As(2)–Si(3)	2.399 (3)	Si(2)–As(2)–Si(3)	94.31 (9)
As(2)–2K	3.482 (3)		
As(3)–2Si(3)	2.370 (2)	Si(1)–As(3)–Si(3)	93.28 (9)
As(3)–Si(1)	2.416 (3)	Si(3)–As(3)–Si(3)	101.3 (1)
K–2As(2)	3.482 (3)	As(2)–K[a]–As(1)	77.71 (5)
K–2As(1)[a]	3.431 (3)	As(2)–K[a]–As(1)[a]	100.95 (5)
K–2As(1)	3.486 (3)	As(1)–K[a]–As(1)[a]	102.67 (5)
Si(1)–Si(2)	2.331 (4)	As(1)–Si(1)–As(1)	103.2 (1)
Si(1)–2As(1)	2.337 (2)	As(1)–Si(1)–As(3)	112.86 (9)
Si(1)–As(3)	2.416 (3)	As(1)–Si(1)–Si(2)	115.3 (1)
Si(1)–2Si(3)	3.480 (4)	As(3)–Si(1)–Si(2)	97.8 (1)
Si(2)–Si(2)	2.322 (6)	As(2)–Si(2)–As(2)	101.2 (1)
Si(2)–Si(1)	2.331 (4)	As(2)–Si(2)–Si(1)	108.2 (1)
Si(2)–2As(2)	2.372 (2)	As(2)–Si(2)–Si(2)	109.1 (1)
Si(2)–2Si(3)	3.497 (4)	Si(1)–Si(2)–Si(2)	119.4 (2)
Si(3)–Si(3)	2.325 (6)	As(2)–Si(3)–As(3)	114.47 (9)
Si(3)–2As(3)	2.370 (2)	As(2)–Si(3)–Si(3)	104.8 (2)
Si(3)–As(2)	2.399 (3)	As(2)–Si(3)–As(3)	101.3 (1)
Si(3)–2Si(1)	3.480 (4)	As(3)–Si(3)–Si(3)	111.0 (1)
Si(3)–2Si(2)	3.497 (4)		

[a] $x + {}^1/_2$, ${}^1/_2 - y$, z.

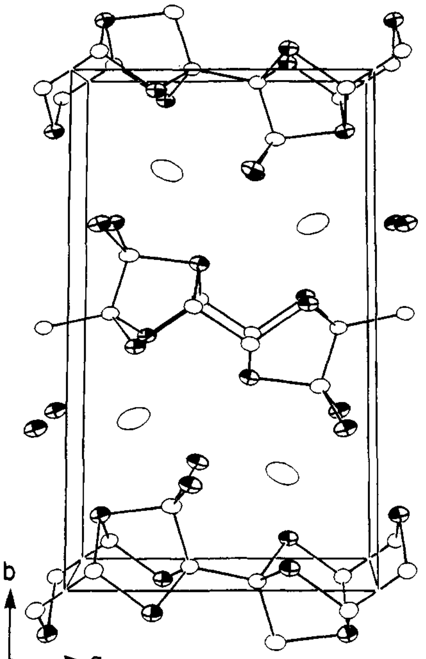

Figure 1. [001] perspective of the unit cell of KSi_3As_3 (space group *Pbam*) with all atoms at $z = 0$ or $^1/_2$: open atoms; Si (in chain) and K; shaded atoms, As (90% probability thermal ellipsoids).

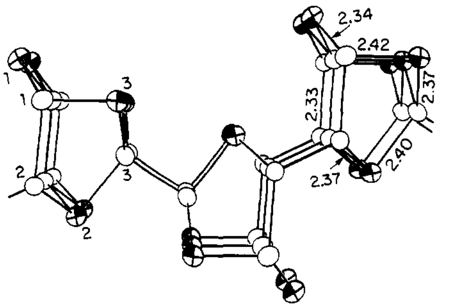

Figure 2. Perspective view of a portion of the $^2_\infty[Si_3As_3]$ layers in KSi_3As_3. Arsenic atoms are shaded.

Structure Description. The unit cell of KSi_3As_3 is depicted in Figure 1 while a portion of the anion layer therein along with some

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Table IV. Silicon–Arsenic Bond Lengths (Å) in Ternary Compounds

compd	Si–As(3b[a])	$Si–As^-(2b)$	$Si–As^{2-}(1b)$	ref
KSi_3As_3	2.372 (2), 2.370 (2), 2.399 (3), 2.416 (3)	2.337 (2)		this work
$Sr_3Si_2As_4$		2.40_2, 2.39_2	2.32_0	16[b]
$Ba_3Si_2As_4$		2.396 (8), 2.416 (8)	2.350 (8)	17
Ba_4SiAs_4			2.407 (5), 2.393 (5)	18[b]

[a] Three-bonded, etc. [b] Refined with isotropic thermal parameters and a limited absorption correction.

bond distances is shown in Figure 2, both in perspective views down the short *c* axis. The layers can be seen to consist of puckered rings of the metalloid elements condensed into chains and then into sheets, or vice versa. Thus, nonplanar five-membered rings consisting of –Si(1,2)As(2)Si(3)As(3)– are condensed into columns or tubes through sharing the last four atoms while the remaining Si(1) atoms are bridged by the exocyclic As(1) atoms. These groups are then joined head-to-head and tail-to-tail into sheets via Si(3)–Si(3) and Si(2)–Si(2) bridges. The last are easier to see in Figures 1 and 2 as the centers of these bonds lie at points of $2/m$ symmetry with the rotation axis normal to the figure. If the construction is instead centered on these Si–Si bonds, **Si**$(3)_{4/2}As(2)_{4/2}As(3)_2$ and **Si(2)**$_2As(2)_{4/2}Si(1)_2[As(1)_{4/2}]As(3)_2$ units of C_{2h} symmetry are joined into strings parallel to [100] via their common As(2) and As(3) atoms and then condensed into sheets along $\vec{c}$. The structural arrangement is very reasonable as it makes all silicon atoms four-bonded and two of the arsenic atoms three-bonded, while the terminal As(1) atoms are only two-bonded. The last are then formally As^-, isoelectronic with selenium. Formulation of the dark purple compound as $K^+Si_3As_3^-$ gives the anion the electron count of a valence (Zintl[6]) compound, and conventional two-center bonding should apply.

Bond Distances. Important distances and angles are listed in Table III, and some distances are marked on Figure 2. Several general points are observed. First, all Si–Si distances are almost the same, the average of 2.326 Å being close to those in many silanes, ~2.34 Å,[15] consistent with the simple bonding expected. All bonds formed by three-bonded arsenic atoms As(2) and As(3) connect to one end of an Si_2 group, and for most of these the bond lengths cluster around 2.38 Å. Different values occur around Si(1). The latter atoms are bridged by the unique, two-bonded As(1) at a shorter 2.337 Å, a normal contraction, while the neighboring Si(1)–As(3) bonds are a somewhat longer 2.416 Å. We suspect that the latter may be induced by strain as the interior angle at Si(1) is only 97.8°. Effects of the polar $(K^+)_{4/4}(As(1)^-)_{4/4}$ interactions (below) may also be important.

Two-bonded arsenic also occurs in the Zintl phases $(M^{II})_3Si_2As_4$, M^{II} = Sr or Ba, where the anion chains contain Si(**As**)As_2Si(**As**) units, four-membered rings condensed at silicon with a terminal arsenic on each.[16,17] Bond distances therein vary in a consistent manner but are uniformly larger than reported here, perhaps because of strain or the larger polarity. The bonds between silicon and the terminal (one-bonded) As^{2-} are now 0.06–0.08 Å less than that to bridging As^-, but the latter average 2.40 Å vs. 2.33 Å in KSi_3As_3. The Si–Si bonds at 2.36 and 2.39 Å ($\sigma \sim 0.01$ Å) likewise average 0.05 Å greater than those in KSi_3As_3. Similarly, $SiAs_4^{8-}$ tetrahedra with only terminal arsenic atoms that occur in Ba_4SiAs_4[18] have the Si–As distances increased to 2.40 Å,[18] perhaps because of the high charge on the anion groups. These data on Si–As distances are summarized in Table IV.

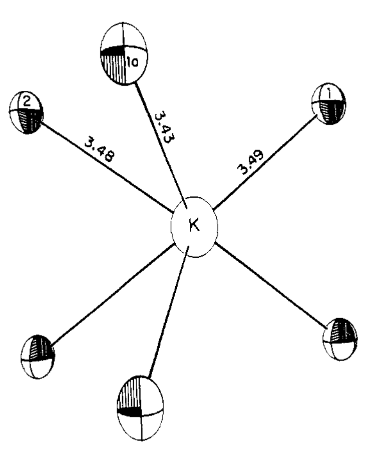

Figure 3. Arsenic environment about potassium in KSi_3As_3. The cation lies on a horizontal mirror plane normal to the figure.

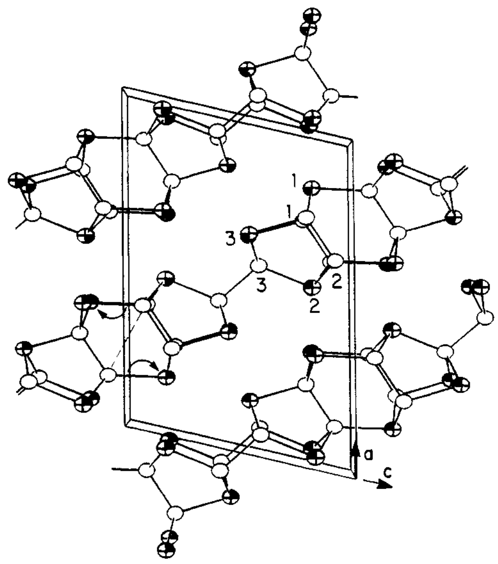

Figure 4. [010] view of the structure of SiAs, space group *C2/m*.[3] Arsenic atoms are shaded. The changes necessary to convert these layers to those in KSi_3As_3 on reduction are depicted in the unit centered around $^1/_4$, $^1/_2$, 0.

The potassium atoms in KSi_3As_3 are coordinated by two pair of the unique As(1) atoms as well as two As(2) atoms from two different layers to give a rather distorted trigonal prismatic environment but one with fairly uniform K–As distances of 3.43–3.49 Å. This unit, as shown in Figure 3, shares both As(1)–As(1) vertical edges and the top and bottom faces with other like prisms so each As(1) has four potassium neighbors and each As(2) has two. The next nearest neighbors, As(3) atoms in the plane of the potassium at 4.22 and 4.37 Å, are disposed on the more open faces of the prism, and their secondary interactions with the cation may be the source of the shortening of two of four of the K–As(1) distances to 3.43 Å.

Cation Exchange. The potassium ions may be readily exchanged by sodium or lithium on reaction with the stoichiometric amount of MI at 500 °C. The crystal ionic radius of sodium is 0.34 Å less than that of potassium,[19] and the decreases observed in *a*, *b*, and *c* on formation of the sodium derivative, ~0.008 (4), 0.60 (3), and 0.016 (1) Å, respectively, are consistent with the layered nature of the structure, Figure 1. The lithium product has a different, unknown structure. The exchange behavior with NaI and LiI and the absence of reaction with RbI and CsI are unusual with regard to the usual course of such reactions that form the small cation–small anion and large cation–large anion pairs. The problem here is somewhat different, however, in that the

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arsenic "anion" separations within the layers are fixed in position. Improved nesting of the sheets and polarization of the arsenic atoms may be involved.

Relationship with Li_3NaSi_6. We have very recently become aware of the existence of a remarkably similar layered anion structure in Li_3NaSi_6.[20] The isoelectric layers there contain the same columns or tubes of shared, five-membered rings, but their interconnection is slightly different. The relative positions of half of the exocyclic bridges are altered in Li_3NaSi_6 as would be accomplished by inverting alternate columns. Thus, the central ring system seen in Figure 2 becomes related to those on both sides by a horizontal screw axis or glide plane centered on the Si(3)–Si(3) connection rather than by the normal twofold axis found at that point with KSi_3As_3. The altered arrangement appears to generate much better cavities along the chain for lithium.

Relationship with SiAs. The structure determined by Wadsten[3] for SiAs in space group $C2/m$ is closely and logically related to that of KSi_3As_3. The former is shown in Figure 4 in the [010] projection. The tricyclic units can be derived from Si_3As_2As rings in KSi_3As_3 by joining these in pairs at the exocyclic As(1) atoms. This generates a pair of puckered five-member rings condensed onto a central six-membered ring at the disilicon edges in the latter. Such a member is centered about a screw axis at $^1/_4$, y, 0 in Figure 4. These ring systems are then linked into strings in the plane of the figure through Si(3)–Si(3) bonds and condensed along $\vec{b}$ to form layers as before. Twofold axes are again found normal to the centers of the Si(3)–Si(3) bonds.

The chemical and structural conversion

$$6SiAs + 2K \rightarrow 2KSi_3As_3 \qquad (2)$$

within one layer of SiAs can be achieved by (1) cleavage of opposite As(1)–Si(2) edges of the six-membered rings to form chains of dibonded As(1) atoms, Figures 1 and 2, and (2), displacement of half of the result by $b/2$ with respect to the other and rotation to allow formation of the Si(2)–Si(2) bonds in KSi_3As_3. The change is depicted symbolically on the same tricyclic unit around $^1/_4$, $^1/_2$, 0 in Figure 4. The direction of opening of these six-membered rings in the conversion to KSi_3As_3 alternates between layers in order to provide good interlayer bonding sites for potassium. It is not obvious, however, that such a reduction (or oxidation) process could actually be achieved in a truly concerted manner. Not surprisingly, KSi_3As_3 and SiAs exhibit very comparable distances as well as similar distributions of angles about equivalent atoms, the latter suggesting somewhat similar strain problems in both structures. The same may pertain to the closely related $GeAs_2$[4] as well.

Further reduction of the anion layers in KSi_3As_3 leads to the chain structure noted before in $Sr_3Si_2As_4$ where the connectivity is $^1_\infty[Si_2(As_2)As_{4/2}]$ via four-membered Si_2As_2 rings. It is interesting that in the related $Sr_3Ge_2As_4$, five-membered $Ge_{1/2}$–Ge–(As_2)–As–$Ge_{1/2}$–As– rings analogous to those found condensed in KSi_3As_3 occur in chains, but with one germanium now common to two rings. The anion structure of KSi_3As_3 was presumably not found during earlier studies with alkaline-earth-metal cations because half as many cations of higher field would not support a stable layered structure.

Acknowledgment. The authors are indebted to Drs. K.-H. Lii and R. Haushalter for early communication of their structural results on KSnAs and KSnSb and to H.-G. von Schnering and R. Nesper for unpublished information on Li_3NaSi_6.

Supplementary Material Available: A listing of anisotropic thermal parameters (1 page); a table of observed and calculated structure factors for KSi_3As_3 (2 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of the Three Geometrical Isomers of (1,3-Propanediamine-*N*,*N'*-diacetato-*N*,*N'*-di-3-propionato)chromate(III). Crystal Structure of *trans*(O_6)-K[Cr(1,3-pddda)]·$3H_2O$

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Chromium(III) complexes with the sexidentate ligand 1,3-propanediamine-*N*,*N'*-diacetate-*N*,*N'*-di-3-propionate (1,3-pddda) were prepared, chromatographically separated into the three geometrical isomers with respect to the N–O chelate ring size (trans(O_5), trans(O_5O_6), and trans(O_6), where O_5 and O_6 refer to the five- and six-membered N–O rings, respectively), and isolated. The X-ray analysis of a crystal from the last-eluted isomer showed the isomer to be *trans*(O_6)-K[Cr(1,3-pddda)]·$3H_2O$, in which the six-membered 3-propionate rings occupy trans-axial sites while the acetate rings lie in the equatorial plane with the two nitrogen atoms. This result confirms the assignment made on the basis of the magnetic circular dichroism and deuteron NMR spectroscopy for the complexes with the 1,3-pddda deuteriated on the methylenes of either the acetate or 3-propionate arms. *trans*(O_6)-K[Cr(1,3-pddda)]·$3H_2O$ ($KCrC_{13}H_{18}N_2O_8$·$3H_2O$) crystallizes in the monoclinic space group $P2_1/a$ with unit cell parameters a = 16.815 (6) Å, b = 11.862 (3) Å, c = 9.449 (3) Å, β = 91.20 (7)°, and Z = 4. The structure converged to R = 0.037 for 2038 reflections.

Introduction

The edta-like ligands (diamine-*N*,*N'*-diacetato-*N*,*N'*-di-3-propionato)chromate(III) might be expected to yield a maximum of three geometric isomers when coordinated as sexidentate chelating agents (Figure 1). Both the trans(O_5) and trans(O_5O_6) isomers have been characterized for cobalt(III) and rhodium(III) complexes of ethylenediamine-*N*,*N'*-diacetate-*N*,*N'*-di-3-propionate (eddda).[2,3] For the eddda–chromium(III) complex, however, only the trans(O_5) isomer has been isolated and identified.[4,5] The favored isomers are those in which the larger six-membered β-alaninate chelate rings are found in the more strained girdling

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