

Fig. 3. Projection along the chain axis of the paraffinic part of (n - $C_{12}H_{25}NH_3$) $_2ZnCl_4$, $a' = 7.20$ Å. *T* and *R* refer to triclinic and orthorhombic contacts according to the nomenclature of Kitaigorodsky.

As shown in Fig. 1, the structure of (n - $C_{12}H_{25}NH_3$) $_2ZnCl_4$ consists of ionic layers sandwiched between layers of paraffinic chains. Unlike (n - $C_{10}H_{21}NH_3$) $_2MnCl_4$, the ionic layers are comprised of single tetrahedral $ZnCl_4^{2-}$ anions in a nearly hexagonal planar array, each $ZnCl_4^{2-}$ anion being surrounded by six NH_3^+ groups. A model of this kind of array is shown in Fig. 2, where all the N—Cl distances shorter than 5 Å are reported.

The Zn—Cl distances are all equal within 0.02 Å and the distortions of the bond angles are less than 5° with respect to the tetrahedral value.

The paraffinic chains have a nearly planar zigzag conformation; the slight distortions of the internal rotation angles from 180° may be due to the need to achieve a closest packing arrangement of the chains in the spatial regions far from the ions. In these regions alternation of *T* and *R* [nomenclature of Kitaigorodsky (1961)] types of side-by-side packing of paraffinic chains is realized, as can be seen in Fig. 3, giving rise locally to a packing density very near that of polyethylene.

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Intermetallic Compounds: Antimony–Beryllium $SbBe_{13}$

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Abstract. $SbBe_{13}$, F.W. 238.88 space group $Fm\bar{3}c$; $a = 10.046(3)$ Å, $Z = 8$; $D_c = 3.13$ g cm $^{-3}$; $U = 1013.9$ Å 3 ; $\mu(Mo K\alpha) = 53.1$ cm $^{-1}$; $F(000) = 688$. This structure was solved by the Patterson method and refined by least-squares analysis to an *R* of 0.043, including 105 reciprocal points. $SbBe_{13}$ has the $NaZn_{13}$ -type structure.

Introduction. This work is part of a structural study of the intermetallic compounds formed by alkaline-earth metals with the Group *Va* elements.

It is well known that Mg reacts with the elements of the *Va* main group giving rise to salt-like structures of the type Mg_3X_2 , where $X = N, P, As, Sb, Bi$ (Stackelberg & Paulus, 1933; Zintl & Husemann,

1933; Martínez-Ripoll, Haase & Brauer, 1974), although von Schnering & Menge (1976) reported a compound with the formula MgP_4 .

The heavy alkaline-earth metals form compounds which deviate from the above-mentioned salt-like stoichiometry [$MX, M_{11}X_{10}, M_5X_3, M_2X$, where $M = Ca, Sr, Ba$ (Iandelli & Franceschi, 1973; Deller & Eisenmann, 1976; Eisenmann & Deller, 1975)], showing their similarity to the divalent lanthanide and actinide elements (Iandelli & Franceschi, 1973; Yoshihara, Taylor, Calvert & Despault, 1975).

The same salt-like formulae as for Mg have been found for several compounds between Be and the Group *Va* elements: Be_3N_2 , Be_3P_2 (Stackelberg & Paulus, 1933) and Be_3As_2 (Weibke, 1930). Baird,

Geach, Knapton & West (1958) observed no reaction between Be and Sb, but evaporation and electrical-resistivity measurements made by Ugai, Gordin & Anokhin (1964) indicate the existence of a compound with the formula Be_3Sb_2 . Our study was undertaken to clarify, by means of X-ray diffraction techniques, the existence of compounds in the Be–Sb system.

A mixture of composition $2\text{Be} + 1\text{Sb}$ in a BeO crucible was placed in an Fe crucible which was closed under Ar. The melt was cooled in two steps, from 1280 to 600°C in 4 h and to room temperature in 14 h.

Single crystals with a metallic appearance were directly isolated from the melt by mechanical fragmentation; three different crystal species were found. Two have cubic symmetry with an F -centred lattice [$a = 6.22$ (1) and 5.91 (1) Å respectively]. A structure determination on the two above-mentioned crystal species was not undertaken because of the poor quality of their single-crystal diffraction patterns. We report here the crystal structure of the third kind of crystal, whose formula was confirmed by this study to be SbBe_{13} .

Crystal data for SbBe_{13} are shown above. Since only a few small single crystals were available, their density could not be exactly measured and only an approximate value ($3.0 \pm 0.1 \text{ g cm}^{-3}$) was determined. A plate-like single crystal of dimensions $0.16 \times 0.11 \times 0.03$ mm was mounted on a Nonius CAD-4 diffractometer. The intensities of 121 independent reflexions were collected in the range $4^\circ < \theta < 37^\circ$ with Mo $K\alpha$ radiation and the $\omega/2\theta$ scan mode. Of these, 105 were considered 'observed' according to the criterion $I > 2\sigma(I)$ and used in the refinement step. Absorption corrections were made with *ORABS* (written by D. Schwarzenbach). Scattering factors for neutral atoms and the anomalous dispersion corrections for Sb were taken from *International Tables for X-ray Crystallography* (1974). A Wilson plot gave the approximate values for the scale and overall temperature factor (0.90 \AA^2). The distribution of maxima in the Patterson function led to the atomic distribution described for the structure of NaZn_{13} (Shoemaker, Marsh, Ewing & Pauling, 1952).

A good weighting scheme for the refinement was found to be $w = w_1 w_2$, where $w_1 = 1/\sigma_1^2$ and $w_2 = 1/\sigma_2^2$ with $\sigma_1 = a + b|F_o|$ and $\sigma_2 = c + d \sin \theta/\lambda$; the coefficients a, b, c, d , given in Table 1, were calculated by *PESOS* (Martinez-Ripoll & Cano, 1975). The refinement was carried out in different steps because of the high correlations among the variables. The following parameters were independently varied: the scale factor; the Sb temperature factor, for reflexions with $\sin \theta/\lambda > 0.6$; the extinction coefficient as an isotropic correction (Larson, 1967); the positional and thermal parameters of Be(2) for only those reflexions with odd indices; and the temperature factor for Be(1) and positional and thermal parameters for Be(2).

Table 1. *Coefficients for the weighting scheme*

	a	b
$0 < F_o \leq 60$	2.98	-0.01
$60 < F_o \leq 165$	1.18	0.02
$165 < F_o \leq 300$	5.32	-0.01
	c	d
$0 < \sin \theta/\lambda \leq 0.63$	5.23	-8.03
$0.63 < \sin \theta/\lambda \leq 0.90$	-2.61	4.41

Table 2. *Atomic parameters for SbBe_{13}*

Standard deviations are given in parentheses. The isotropic extinction coefficient = $2.1(1) \times 10^{-3}$.

	x	y	z	B (Å ²)
Sb	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0.84 (1)
Be(1)	0	0	0	0.1 (2)
Be(2)	0	0.1781 (5)	0.1157 (5)	0.22 (6)

The above-mentioned refinement scheme was repeated once and led to the atomic parameters given in Table 2. The unweighted and weighted disagreement indices are $R = 0.043$ and $R_w = 0.050$, where $R_w = (\sum w\Delta^2 / \sum w|F_o|^2)^{1/2}$.*

Discussion. The existence of the intermetallic compounds of the series AB_{13} has already been reported (Ketelaar, 1937; Zintl & Hauke, 1937, 1938; Shoemaker, Marsh, Ewing & Pauling, 1952). Be reacts with many metals of the Groups IIa, IVb and IIIb (including the lanthanides and actinides) to form compounds corresponding to the formula AB_{13} , where $A = \text{Mg, Ca, Sr, Sc, Y, La, Ln, An, Zr, Hf}$ (Ln = lanthanides, An = actinides). This structure type occurs between elements with metallic-radii ratios (r_{Be}/r_A) ranging from 0.523 (SrBe_{13}) to 0.741 (UBe_{13}). Also the compounds (Na, K, Ca, Sr, Ba) Zn_{13} and (K, Rb, Cs) Cd_{13} present metallic-radii ratios within the range mentioned above [references for these and for the AB_{13} compounds are to be found in Benedict, Buijs, Dufour & Toussaint (1975) and *Landolt-Börnstein* (1971)].

The first example of an AB_{13} structure involving a Group Va element is the present compound SbBe_{13} , with a radii ratio of 0.706. If the radii ratio is a factor

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32139 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

determinant of this structure type, one could also expect the existence of the compound BiBe_{13} (radii ratio = 0.661).

In Fig. 1 are plotted the positional parameters y and z for SbBe_{13} , together with those for NaZn_{13} (Shoemaker, Marsh, Ewing & Pauling, 1952), MgBe_{13} and CaBe_{13} (Baker, 1962). It is seen that the parameter values obtained for all these structures differ considerably from the values required either by a regular icosahedron or by a regular snub cube.

The bond distances in SbBe_{13} are reported in Table 3. The shortest $\text{Be}(2)\text{--Be}(2)$ distances of 2.133 Å are shorter than the values of 2.225 and 2.286 Å for Be. Similar discrepancies were found in the structures of MgBe_{13} and CaBe_{13} (Baker, 1962), where the shortest $\text{Be}(2)\text{--Be}(2)$ distances are 2.158 and 2.161 Å respectively. SbBe_{13} presents a 'volume contraction' of ~6% when the volume per formula unit of the compound is compared with the volume of the component metals

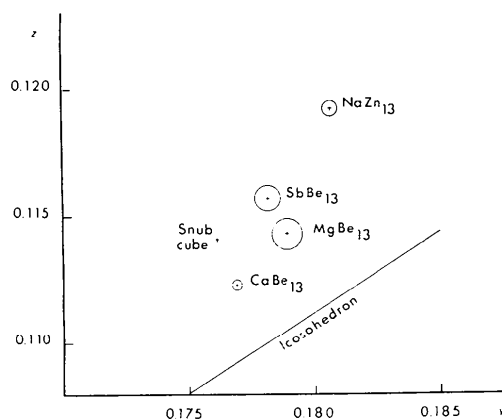


Fig. 1. Positional parameters z versus y . The radii of the circles represent the standard deviations for the determinations concerned.

Table 3. Bond lengths in SbBe_{13}

Estimated standard deviations are given in parentheses.

		d (Å)	Number of bonds
Bonds involving Be(1) (0,0,0)			
Be(2)	(0, y, z)	2.133 (5)	12
Bonds involving Be(2) (0, y, z)			
Be(1)	(0,0,0)	2.133 (5)	1
Be(2)	(0, $z, \frac{1}{2} - y$)	2.165 (7)	2
Be(2)	($z, \frac{1}{2} - y, 0$)	2.188 (6)	2
Be(2)	($z, 0, y$)	2.224 (5)	4
Be(2)	(0, $y, -z$)	2.324 (7)	1
Sb	($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$)	2.941 (3)	2
Bonds involving Sb ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$)			
Be(2)	(0, y, z)	2.941 (3)	24

computed in the correct stoichiometry. This can be due to an electron transfer (Pauling, 1950).

All calculations were made with the X-RAY 70 system (Stewart, Kundell & Baldwin, 1970) running on the Univac 1106 computer of the University of Freiburg, Germany.

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