Structure of Complexes Formed by Pyridine with Cyanogen Iodide and Iodomonobromide

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X-Ray investigations of solid 1:1 compounds containing pyridine or its homologues and iodine or interhalogen molecules have shown that the complexes tend to be planar with a linear arrangement nitrogen-halogen-halogen. In all investigated complexes the N···I bond had a length of 2.3 Å.[1]

According to liquid phase spectroscopic measurements cyanogen iodide is a much weaker acceptor than, *e.g.*, iodomonochloride or iodine and we wanted to state if the N···I distance in its solid pyridine compound is appreciably larger than 2.3 Å. We prepared the solid compound and eventually succeeded in preparing single crystals which could be used in a two-dimensional structure analysis. The expected 1:1 composition was confirmed by chemical analysis (theoretical values in parenthesis): (C 31.26 % (31.0); H 2.31 % (2.2); N 10.30 % (12.0); I 55.89 % (54.7)). The *monoclinic* crystals belong to the space group $C2/c$ and the unit cell containing *four* formula units has the parameters:

$a = 9.30$ Å; $b = 12.12$ Å; $c = 7.57$ Å; $\beta = 109°$.

The space group $C2/c$ requires the complex to have $C2$ symmetry and the cyanogen iodide atoms to be situated on the line joining the N and γ C atoms of the pyridine molecule. The N···I bond is 2.57 ± 0.02 Å long and therefore significantly longer than 2.3 Å. A Fourier projection along [001] is reproduced in Fig. 1.

It has been stated [2] that the iodomonobromide-pyridine compound is isomorphous with the iodomonochloride compound. We now report some details from a two-dimensional analysis of the former:

$a = 4.386$ Å; $b = 12.637$ Å; $c = 14.208$ Å; $\beta = 97.4°$.

The N···I—Br arrangement is nearly linear, the N···I distance equal to $2.26 \pm$

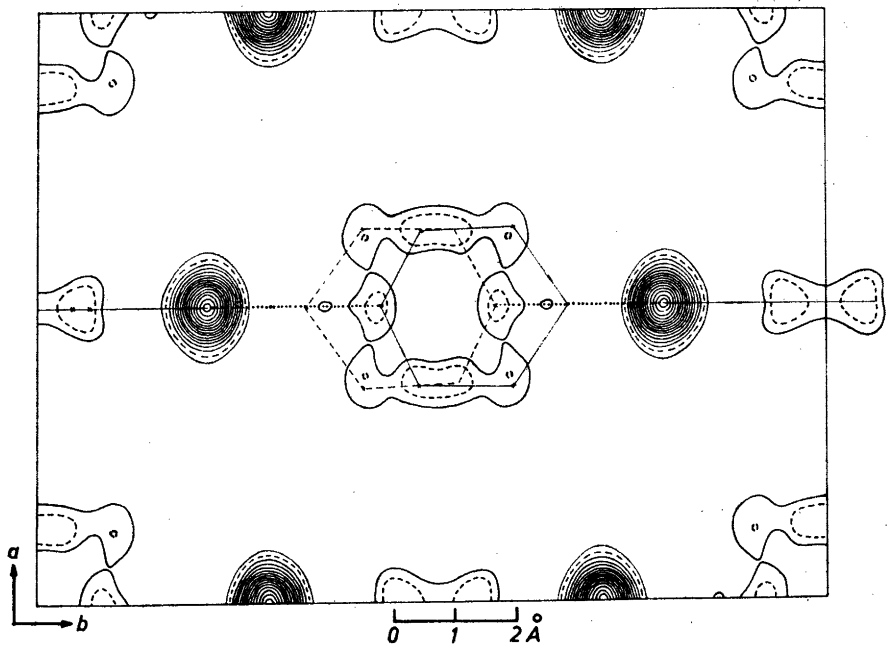

Fig. 1.

0.04 Å and the I—Br bond distance to 2.66 ± 0.01 Å. The lengthening of the I—Br bond distance relative to that observed in the free IBr molecule (2.47 Å) conforms well to those found in I_2 and ICl complexes previously investigated.

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2. Hassel, O. and Rømming, Chr. *Acta Chem. Scand.* **10** (1956) 696.

Received January 28, 1967.

The Crystal Structures of SiP_2, $SiAs_2$, and GeP

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In a recent paper by Hulliger and Mooser [1] data are given on the electric conductivities of several binary phases containing elements of the fourth and the fifth group of the periodic system. Among these compounds which are all reported to be semiconductors are several phases of AB and AB_2 stoichiometry. By analogy with structural data previously reported for $GeAs_2$[2] these authors also discuss structural properties and in particular suggest probable atomic coordinations in such phases, *viz.* $SiAs_2$,[3] GeP,[4] SiAs,[3] and GeAs.[5]

The structure of SiAs [6] was recently reported by the present author. The layer structure found for this compound was actually found to be analogous to that of GeAs, independently derived by Bryden. The latter author also determined the structure of $GeAs_2$ (*cf.* above).

In the present investigation some further preparative and structural studies have been performed on the AB and AB_2 phases. The syntheses were carried out in evacuated silica tubes with stoichiometric mixtures of high purity samples of the elements. Red phosphorus was used to prepare the phosphides. The tubes were heated in a furnace with a temperature gradient with the high-temperature end around 900°C and the low-temperature end somewhat above the condensation point of the group five element. In this way deposits of the binary compounds grew in the low-temperature region of the reaction tube.

Using this technique it was possible to prepare not only several previously known phases, *viz.* GeP, SiAs, GeAs, $SiAs_2$, and $GeAs_2$ but also SiP_2 which has not been reported in the literature. All the phases were obtained as needle-shaped crystals often up to several tenths of a millimeter in length.

The products were investigated by taking X-ray powder and Weissenberg photographs. In this way it was possible to assign them to the structural types given in Table 1. The unit cell parameters were obtained from Guinier powder patterns registered with potassium chloride (a = 6.2930 Å) added to the specimens as an internal standard.

The $GeAs_2$(AB_2) and SiAs(AB) structure types are built in layers with weak bonds between the layers. The coordination around the A atoms is normal in both structures, *i.e.* four. This is obviously in agreement with the suggestions by Hulliger and Mooser. In the $GeAs_2$-type the A atoms have four tetrahedral B atom neighbours, while in the SiAs-type the A atoms are surrounded by a tetrahedron of three B and one A atom. The $GeAs_2$-type has an arrangement of AB_4 tetrahedra sharing three corners and a B—B bond equal to the "metallic" distance. This sort

Table 1.

	Structure type	a Å	b Å	c Å	β	Z	Space group
SiP_2	$GeAs_2$	13.97	10.08	3.436		8	*Pbam*
$SiAs_2$	»	14.53	10.37	3.636		8	*Pbam*
$GeAs_2$	»	14.76	10.16	3.728		8	*Pbam*
GeP	SiAs	15.14	3.638	9.19	101.1°	12	*C2/m*
SiAs	»	15.98	3.668	9.53	106.0°	12	*C2/m*
GeAs	»	15.59	3.792	9.49	101.3°	12	*C2/m*