

CRYSTALLOGRAPHY

Arsenides and Antimonides of Niobium

THE phase relationships in the systems niobium-arsenic and niobium-antimony have been studied by X-ray methods. Density determinations and magnetic susceptibility measurements have been carried out.

The existence of the Nb₃Sb phase reported by Matthias *et al.*¹, Wood *et al.*² and Nevitt³ has been confirmed. The NbAs phase has independently been examined by Boller and Parthé⁴ and by us. The occurrence of three other previously unknown phases, the Nb₅Sb₄, NbAs₂ and NbSb₂ phases, have been established.

The lattice dimensions and observed densities are:

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°) or <i>c/a</i>	<i>d</i> _{pycn} (g cm ⁻³)
NbAs	3.4517		11.680	3.3838	7.93
NbAs ₂	9.357	3.3823	7.792	119.46	7.41
Nb ₃ Sb	5.2643				8.83
Nb ₅ Sb ₄	10.314		3.556	0.3448	8.17
NbSb ₂	10.239	3.6319	8.833	120.07	8.22

As the lattice constants are almost invariable for specimens with different initial proportions of the components no composition ranges of the phases are indicated.

The crystal structures, that is, types or space groups and parameters, are:

NbAs: Space group *I*4₁ or *I*4₁*md*
4 Nb and As in (*a*)
Nb: *z* = 0; As: *z* = 0.416 ± 0.001

NbAs₂: Space group *C*2
4 Nb, As_I and As_{II} in (*c*)

	<i>x</i>	<i>y</i>	<i>z</i>
Nb	0.3444	$\frac{1}{2}$	0.3044
As _I	0.0948	0.488	0.3928
As _{II}	0.1899	0.067	0.0257

Nb₃Sb: β -W type
Nb₅Sb₄: Ti₅Te₄ type
NbSb₂: Space group *C*2
4 Nb, Sb_I and Sb_{II} in (*c*)

	<i>x</i>	<i>y</i>	<i>z</i>
Nb	0.343	$\frac{1}{2}$	0.304
Sb _I	0.096	0.5	0.393
Sb _{II}	0.142	0.0	0.027

NbAs, NbAs₂ and NbSb₂ have diamagnetic susceptibilities, whereas Nb₃Sb and Nb₅Sb₄ show weak temperature independent paramagnetism.

Details of the structures and discussion of the chemical bonding will be published elsewhere.

We thank Prof. Haakon Haraldsen for his advice.

Note added in proof. Since this communication was submitted for publication an independent confirmation of the existence of the NbAs and NbAs₂ phases has been published by Saini *et al.*⁵

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¹ Matthias, B. T., Wood, E. A., Corenzwit, E., and Bala, V. B., *J. Phys. Chem. Solids*, **1**, 188 (1956).

² Wood, E. A., Compton, V. B., Matthias, B. T., and Corenzwit, E., *Acta Cryst.*, **11**, 604 (1958).

³ Nevitt, M. V., *Trans. Met. Soc., Amer. Inst. Mech. Eng.*, **212**, 350 (1958).

⁴ Boller, H., and Parthé, E., *Acta Cryst.*, **16**, 1095 (1963).

⁵ Saini, G. S., Calvert, L. J. D., and Taylor, J. B., *Canad. J. Chem.*, **42**, 630 (1964).

Crystal and Molecular Structure of 1,3-Dihydro-1-hydroxy-3-oxo-1,2-benziodoxole

O-IODOSOBENZOIC acid (*I*) has been recognized as an atypical compound ever since it was first synthesized¹. Askenasy and Meyer² suggested that this compound existed as a 5-membered heterocyclic ring. This cyclic configuration was substantiated by the infra-red studies of Bell and Morgan³. Further evidence favouring the

heterocyclic ring structure was offered by Wolf and Hsu⁴, who synthesized homologues of (*I*) with 6- and 7-membered heterocyclic rings. In view of the lack of information concerning the chemical bonding of the iodine in these heterocyclic compounds, the present X-ray investigation of (*I*) was undertaken.

(*I*) crystallizes from water as fine monoclinic needles elongated along the *b* axis. The following crystallographic data were obtained for these crystals:

$$\begin{aligned} a_0 &= 12.89 \pm 0.01 \text{ \AA} & Z &= 4 \\ b_0 &= 4.10 \pm 0.02 \text{ \AA} & \rho_{\text{obs}} &= 2.38 \pm 0.03 \text{ g cm}^{-3} \\ c_0 &= 14.05 \pm 0.01 \text{ \AA} & \rho_{\text{cal}} &= 2.33 \pm 0.01 \text{ g cm}^{-3} \\ \beta &= 96.73 \pm 0.05^\circ & \text{Space group} &= P2_1/c \end{aligned}$$

Three layers of Weissenberg intensity results were obtained with copper *K* α -radiation from a crystal mounted along *b*. The intensities of 520 independent reflexions were measured from these photographs, in part with a micro-densitometer and in part visually. The intensity results were converted to *F*² in the usual manner. Absorption corrections were not made because the crystal was only 0.06 mm in diameter. The structure factors were initially scaled together by means of *h**k*0 and 0*kl* precession data, and the interlayer scaling was further improved during the final stages of least-squares refinement.

The co-ordinates of the 11 atoms in this structure were readily obtained from 3-dimensional Patterson and Fourier syntheses. The refinement of these parameters was carried out isotropically by least squares, minimizing the function $\sum w (|F_o| - G |F_c|)^2$. The *R* value (the usual discrepancy index) was 13.7 per cent after 5 cycles of refinement.

Fig. 1 is a view of (*I*) as it appears down the *b* axis. The features of major interest in this structure are:

(1) The C(1)—I, O(3)—I and O(2)—I bond distances are 2.16, 2.00 and 2.30 ± 0.05 Å respectively. The first two of these are in agreement with the sum of the covalent radii, 2.1 and 2.0 Å (ref. 5), respectively. The greater length observed for the I—O(2) bond may possibly be due to steric strain in the molecule and/or a greater amount of ionic character in this bond over the normal covalent bond.

(2) The O(2)—I—C(1) and O(3)—I—C(1) angles are 77° and 89° ± 4° respectively. These angles are similar in magnitude to those reported by Archer and Van Schalkwyk⁶

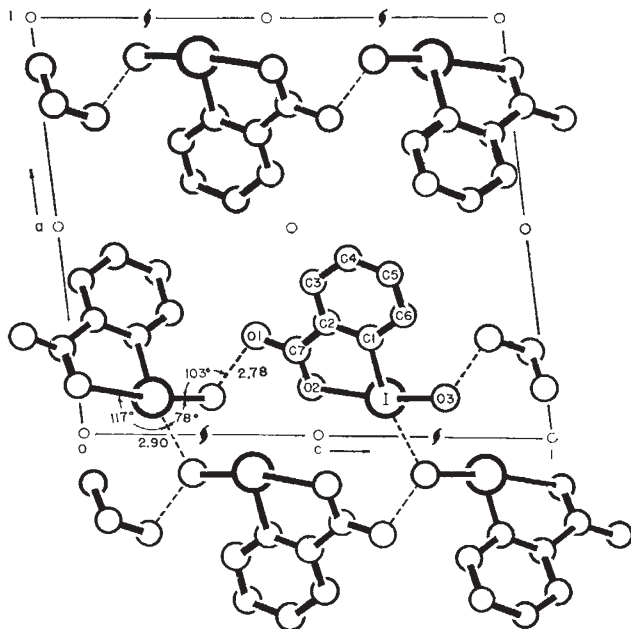


Fig. 1