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**The structure of 5-chlorosalicylaldoxime.** By S. H. SIMONSEN and C. E. PFLUGER,\* *Department of Chemistry, The University of Texas, Austin, Texas, U.S.A.*

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In connection with an investigation of the structure of palladium(II) salicylaldoxime it was desirable to ascertain the distortion of the salicylaldoxime molecule upon formation of the palladium complex. 5-Chlorosalicylaldoxime was prepared because the presence of the heavy atom would facilitate the determination without appreciably affecting the structure of the salicylaldoxime molecule.

Suitable crystals of 5-chlorosalicylaldoxime were obtained by slow cooling of a saturated aqueous solution, and by evaporation of a chloroform solution. The unit cell is monoclinic with:

$$a = 13.69, b = 3.90, c = 14.35 \text{ \AA}; \beta = 100.0^\circ.$$

Characteristic extinctions were noted which are those required by the space group  $P2_1/a$ , and the unit cell contains four molecules. Density: calculated, 1.510 g.cm.<sup>-3</sup>; measured (by flotation), 1.510 g.cm.<sup>-3</sup>.

Intensity data for the ( $h0l$ ) zone were collected from Weissenberg photographs. The approximate structure was determined by a Patterson function projected along [010], which showed directly the outline of the molecule. Several electron-density projections were calculated, and back-shift corrections were made. At this stage of refinement, the agreement index,  $R$ , between calculated and observed structure factors was 16% (233 ( $h0l$ ) reflections). Further refinement of the structure by least squares is in progress, and intensity data for the ( $0kl$ ) zone are being collected.

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It was evident by the shortening of the benzene bond lengths in the projection that the molecules were tilted out of the (010) plane. Using the accepted value of 1.39 Å, the angle of tilt was calculated to be 27° 46' about an axis lying in the (010) plane and making an angle of 69° 15' with [100]. The bond lengths, calculated using the above tilt, were in good agreement with the values reported by Jerslev (1950) for *syn-p*-chlorobenzaloxime, and are given in Table 1.

Table 1. Comparison of observed bond lengths of *syn-p*-chlorobenzaloxime and 5-chlorosalicylaldoxime

Bond	<i>syn-p</i> -Chlorobenzaloxime	5-Chlorosalicylaldoxime
C-C in benzene ring	1.35-1.38 Å	1.38-1.40 Å
C-Cl	1.78	1.82
C(benzene)-CH	1.45	1.43
CH-N	1.31	1.25
N-O	1.36	1.40

The short CH-N and long N-O distances may be due to the N-O group being tilted slightly out of the plane of the Cl and C atoms. Full details of the structure will be reported at a later date.

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**Orientation relationships involved in the formation of  $\alpha$ -W<sub>2</sub>C on tungsten.** By R. A. SWALIN,\* *General Electric Research Laboratory, Schenectady, N. Y., U.S.A.*

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In the study reported here, tungsten wires with a diameter of 0.025 cm. which had been previously coated with a thin film of graphite were annealed *in vacuo* at elevated temperatures and investigated using X-ray diffraction techniques. In Fig. 1(a) is shown the X-ray pattern from a wire sample which had been annealed at 1750° C. for 10 min. The pattern was obtained using a flat-plate front-reflection camera with a specimen-film distance of 5 cm. Molybdenum radiation was employed in conjunction with a zirconium filter. All the diffraction rings in Fig. 1(a) match closely with those of tungsten. From the intensity maxima on the diffraction rings, it

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can be deduced that the wire has a strong  $\langle 110 \rangle$  texture. It has also been shown that the crystals on the surface of the wire are oriented with a  $\{100\}$  plane tangential to the surface and that the  $\langle 110 \rangle$  texture is maintained at least up to 2050° C. (Swalin & Geisler, 1957). The size and shape of the crystals has been determined microscopically and were found to have the shape of long fibers oriented parallel to the wire axis with a diameter of about 10<sup>-4</sup> cm.

In Fig. 1(b) is shown an X-ray pattern for a wire sample which had been annealed at 1850° C. for 10 min. The other conditions were the same as for Fig. 1(a). Interpretation of this pattern shows that the diffraction rings are representative of  $\alpha$ -W<sub>2</sub>C with a few weak tungsten lines included. A W<sub>2</sub>C film of a few microns thickness

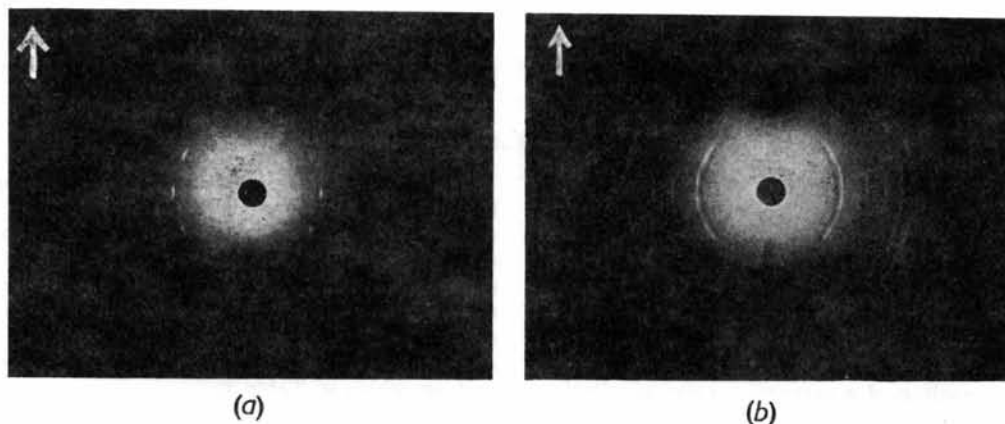


Fig. 1. X-ray pattern of graphite-coated tungsten wire which has been annealed (a) at 1750°C., (b) at 1850°C. Arrows are parallel to wire axis.

is enough to prevent a significant contribution from the tungsten substrate to the pattern.  $\alpha$ -W<sub>2</sub>C has been shown to have a hexagonal structure in which the tungsten atoms are arranged in close-packed fashion; the lattice parameters of the unit cell are

$$a = 2.99, c = 4.71 \text{ \AA}$$

(Smithells, 1952). In Table 1, some of the low-index

Table 1. Diffraction analysis of Fig. 1(b)

Planar spacing				
Measured	Calc. for $\alpha$ -W <sub>2</sub> C	Calc. for W	Plane	
2.56 Å	2.59 Å (50)	—	10.0	W <sub>2</sub> C
2.34	2.36 (40)	—	00.2	W <sub>2</sub> C
2.25	2.24 (100)	2.27 Å (100)	{ 10.1 110	{ W <sub>2</sub> C W
2.22	—	—	—	—
1.73	1.74 (40)	—	10.2	W <sub>2</sub> C
1.57	—	1.58 (15)	200	W
1.49	1.49 (60)	—	11.0	W <sub>2</sub> C
1.34	1.34 (50)	—	10.3	W <sub>2</sub> C

Numbers in parentheses indicate relative intensities.

planes giving rise to diffraction rings in Fig. 1(b) are identified.

Analysis of Fig. 1(b) by means of stereographic projection techniques indicate that the  $\alpha$ -W<sub>2</sub>C crystals on the surface of the wire exist in three preferred orientations relative to the fiber axis of the tungsten wire. These three preferred orientations were found to be those in which {00.1}, {22.3}, and {10.0} poles of W<sub>2</sub>C crystals occurred parallel to the <110> fiber axis of the tungsten wire. These orientation relationships indicate further that {00.1} planes of W<sub>2</sub>C crystals are inclined at 0°, 30°, and 90° to the fiber axis of the wire. Since {110} planes of the tungsten substrate are also inclined at 0°, 30°, and 90° to the fiber axis, as shown by the strong <110> fiber texture, it is concluded that {00.1} planes of  $\alpha$ -W<sub>2</sub>C exist parallel to {110} planes of the tungsten substrate. Stereographic analysis also indicates that the <10.0> direction of  $\alpha$ -W<sub>2</sub>C crystals is parallel to the <110> direction of the tungsten substrate. Since tungsten atoms on the {00.1} planes of  $\alpha$ -W<sub>2</sub>C match very closely with

atoms on {110} planes of tungsten with respect to spacing and angular relationships when  $\langle 10.0 \rangle_{W_2C} \parallel \langle 110 \rangle_W$ , these results suggest that the {110} planes of tungsten represent the conjugate plane for the formation of  $\alpha$ -W<sub>2</sub>C. The relation between atoms on these planes is shown quantitatively in Fig. 2. It is noted in this con-

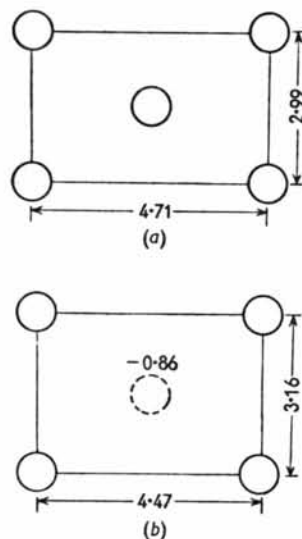


Fig. 2. Atom spacings on (a) (10.0) plane of  $\alpha$ -W<sub>2</sub>C and (b) (110) plane of W. Values are in Ångström units.

nection that the orientation relationship reported here is the same as that found by Burgers (1934) in the case of the b.c.c.  $\rightarrow$  h.c.p. transformation in zirconium. The analogy is very close since, as mentioned earlier, the tungsten atoms in hexagonal  $\alpha$ -W<sub>2</sub>C are arranged in h.c.p. fashion with the carbon in the interstices.

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