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The crystal structure of Cr₂₃C₆.* By A. L. BOWMAN, G. P. ARNOLD, E. K. STORMS and N. G. NERESON, *Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544, U.S.A.*

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The crystal structure of Cr₂₃C₆ is cubic, space group *Fm3m*, $a_0 = 10.650$, 4Cr in (*a*) (000), 8Cr in (*c*) ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$), 48Cr in (*h*) (0*xx*), $x = 0.1699$, 32Cr in (*f*) (*xxx*), $x = 0.3809$, 24C in (*e*) (*x*00), $x = 0.2765$, based on neutron diffraction data from a powder sample.

The crystal structure of chromium carbide, Cr₂₃C₆, has been described as cubic, space group *Fm3m*, 4Cr (I) in (*a*) (000), 8Cr (II) in (*c*) ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$), 48Cr (III) in (*h*) (0*xx*), $x = 0.165$, 32Cr (IV) in (*f*) (*xxx*), $x = 0.385$, 24C in (*e*) (*x*00), $x = 0.275$ (Westgren, 1933) on the basis of X-ray single crystal and powder diffraction data. We have confirmed this structure and determined the atom positions more precisely by a neutron diffraction study of a powder sample.

Chromium carbide was prepared by arc-melting the high-purity elements under argon. The arc-cast material was ground to -250 mesh and used without further heat

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treatment. The X-ray and neutron diffraction patterns show Cr₂₃C₆, $a_0 = 10.650 \pm 0.002$ Å and a small chromium impurity phase, $a_0 = 2.885 \pm 0.001$ Å. Neutron diffraction data were obtained at the Los Alamos West Omega Reactor, scanning from $2\theta = 5$ to 70° at an interval of 0.05° , at a wavelength of 1.3366 Å. The sample was contained in a parallel-sided holder made from (Ti-Zr) null-matrix alloy and was placed in the symmetrical transmission position. An absorption parameter of $\mu t = 0.168$ was measured.

The observed intensities were determined by least-squares analysis of the diffraction data, and were fitted to the trial structure by least-squares solution of the equation (Bacon, 1962)

$$I = K \frac{\exp(-\mu t \sec \theta)}{\sin^2 2\theta} \cdot \exp\left(-2B \frac{\sin^2 \theta}{\lambda^2}\right) jF^2,$$

Table 1. Summary of experimental data

<i>hkl</i>	<i>d</i>	<i>I</i> (obs)	<i>I</i> (calc)
111	6.26	0.7	0.8
200	5.32	2.7	3.0
220	3.76	3.1	3.3
311	3.21	0.9	0.7
222	3.07	9.4	8.5
400	2.67	2.9	2.7
331	2.44	0.5	0.8
420	2.36	0.7	0.4
422	2.17	0.7	0.6
511 } 333 }	2.00	28.7	25.9
440	1.88	22.4	23.2
531	1.80	11.9	12.3
600 } 442 }	1.78	9.5	9.7
620	1.68	0.1	0.1
533	1.62	0.9	1.5
622	1.61	19.5	19.3
444	1.54	1.3	1.4
711 } 551 }	1.490	4.4	4.1
640	1.476	2.9	3.4
642	1.421	1.1	1.0
731 } 853 }	1.386	4.4	4.4
800	1.332	6.0	6.5
733	1.302	4.5	4.3
820 } 644 }	1.287	0.9	0.7
822 } 660 }	1.256	8.5	8.2
751 } 555 }	1.230	5.4	5.5
662	1.222	6.2	5.5
840	1.191	0.4	0.0
911 } 753 }	1.167	7.9	7.8

with $K = 0.0017 \pm 0.0001$, $B = 0.41 \pm 0.15$, $x_{\text{Cr(III)}} = 0.1699 \pm 0.0004$, $x_{\text{Cr(IV)}} = 0.3809 \pm 0.0005$, $x_c = 0.2765 \pm 0.0005$, $R = 0.056$, where $R = \sum w|I_o - I_c| / \sum wI_o$. Neutron scattering lengths were 0.352×10^{-12} cm for chromium and 0.665×10^{-12} cm for carbon. The observed and calculated neutron diffraction intensities are compared in Table 1.

The Cr₂₃C₆ structure was originally described in terms of NaCl-type packing of cubo-octahedra [12Cr(III) with a Cr(I) in the center] and cubes 8Cr(IV) (Westgren, 1933). The cubo-octahedra are regular, with a radius of 2.56 Å and Cr-Cr distances of 2.56 Å on the surface, while the Cr₈ cubes have an edge length of 2.54 Å. Each cubo-octahedron is bonded to its eight neighbor cubo-octahedra through Cr-Cr bonds of 2.41 Å. Each cube is bonded to its eight neighbor cubes through the Cr(II) in the center of each octant, again with Cr-Cr bonds of 2.41 Å, with the Cr(II) acting as a bridging atom. The cubo-octahedra and cubes are bonded together through the carbon atoms,

Table 2. Interatomic distances

Cr(I) — Cr(III)	(12)	2.558 (5)
Cr(II) — Cr(IV)	(4)	2.415 (5)
Cr(II) — Cr(III)	(12)	2.923 (2)
Cr(III) — Cr(III)	(1)	2.414 (9)
	(4)	2.558 (5)
Cr(III) — Cr(I)	(1)	2.558 (5)
Cr(III) — Cr(II)	(2)	2.923 (2)
Cr(III) — Cr(IV)	(4)	2.637 (7)
Cr(III) — C	(2)	2.136 (5)
Cr(IV) — Cr(II)	(1)	2.415 (5)
Cr(IV) — Cr(IV)	(3)	2.536 (11)
Cr(IV) — Cr(III)	(6)	2.637 (7)
Cr(IV) — C	(3)	2.110 (6)
C — Cr(III)	(4)	2.136 (5)
C — Cr(IV)	(4)	2.110 (6)

along the $\langle 100 \rangle$ directions, with a Cr-C distance of about 2.12 Å. The interatomic distances are listed in Table 2. The Cr coordination about the carbon atom is an 8-fold square anti-prism, with the carbon atom displaced slightly from the center.

The compounds which form in this structure type have been reviewed recently (Stadelmaier, 1969). They include Cr_{23}C_6 , Mn_{23}C_6 , and many ternary carbides and borides.

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For estriol, $\varphi_{200} = 0$. By HERBERT HAUPTMAN, *Medical Foundation of Buffalo, 73 High Street, Buffalo, New York 14203, U.S.A.*

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It is shown that the value of the important phase φ_{200} for estriol is zero.

The estriol structure ($\text{C}_{18}\text{H}_{24}\text{O}_3$, $P2_1$, $Z=4$) was the first to be solved *via* the least-squares analysis of the cosine invariants (Hauptman, Fisher, Hancock & Norton, 1969). The phase $\varphi_{200} = 0$ was one of five in the basic set but its value was not unambiguously determined by means of \sum_1 . Nevertheless its value was well determined by an argument which the reader is challenged to supply and which depends on the facts that $|E_{200}| = 5.40$, $|E_{100}| = 0.00$, and that there are two molecules in the asymmetric unit. Since the appearance of this challenge no one has responded to it, but some have questioned the existence of such an argument (*e.g.* Woolfson, 1971, p. 428). It therefore seems appropriate to present this brief analysis, especially since it may well have more general applicability.

First, the fact that the low angle $|F_{100}|^2$ was measured to be zero (not merely small) must surely have a fundamental structural significance. Next, ignoring the negligible contribution of the hydrogen atoms,

$$E_{200} = \frac{2}{\sqrt{84}} \sum_{\mu=1}^{42} \cos 4\pi x_{\mu}, \quad (1)$$

where the x_{μ} are the x coordinates of the 42 independent nonhydrogen atoms. Only if either

$$x_{\mu} = 0 \text{ or } \frac{1}{2}, \mu = 1, \dots, 42, \quad (2)$$

or

$$x_{\mu} = \pm \frac{1}{4}, \mu = 1, \dots, 42, \quad (3)$$

would $|E_{200}|$ attain the maximum possible value of $84^{1/2} \approx 9.17$. However $|E_{200}|$ is in fact equal to 5.40, large enough to imply that either (2) holds or (3) holds, approximately. Since there are two independent molecules, each approximately planar, in the asymmetric unit, it readily follows that either

$$\left. \begin{aligned} x_{\mu} &= \varepsilon_{\mu}, \mu = 1, \dots, 21; \text{ molecule I,} \\ x_{\mu} &= \frac{1}{2} + \varepsilon_{\mu}, \mu = 22, \dots, 42; \text{ molecule II,} \end{aligned} \right\} \quad (4)$$

or

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$$\left. \begin{aligned} x_{\mu} &= \frac{1}{4} + \varepsilon_{\mu}, \mu = 1, \dots, 21; \text{ molecule I,} \\ x_{\mu} &= -\frac{1}{4} + \varepsilon_{\mu}, \mu = 22, \dots, 42; \text{ molecule II,} \end{aligned} \right\} \quad (5)$$

where the magnitudes of most of the ε_{μ} are small.

Next,

$$E_{100} = \frac{2}{\sqrt{84}} \sum_{\mu=1}^{42} \cos 2\pi x_{\mu} \quad (6)$$

and, according as (4) or (5) holds, either

$$E_{100} \approx \frac{2}{\sqrt{84}} \left\{ \sum_{\mu=1}^{21} \left(1 - \frac{\varepsilon_{\mu}^2}{2} \right) - \sum_{\mu=22}^{42} \left(1 - \frac{\varepsilon_{\mu}^2}{2} \right) \right\} \quad (7)$$

or

$$E_{100} \approx \frac{2}{\sqrt{84}} \left\{ \sum_{\mu=1}^{21} \varepsilon_{\mu} - \sum_{\mu=22}^{42} \varepsilon_{\mu} \right\}, \quad (8)$$

i.e. either

$$E_{100} \approx -\frac{1}{\sqrt{84}} \left\{ \sum_{\mu=1}^{21} \varepsilon_{\mu}^2 - \sum_{\mu=22}^{42} \varepsilon_{\mu}^2 \right\}, \quad (9)$$

or

$$E_{100} \approx \frac{2}{\sqrt{84}} \left\{ \sum_{\mu=1}^{21} \varepsilon_{\mu} - \sum_{\mu=22}^{42} \varepsilon_{\mu} \right\}. \quad (10)$$

Taking into account the fact that the magnitudes of the ε_{μ} are small, inspection of (9) and (10) clearly shows that it is (9), rather than (10), which is consistent with the observed value of zero for $|E_{100}|$. It follows that (4), not (5), holds so that (1) implies

$$E_{200} > 0 \quad (11)$$

or

$$\varphi_{200} = 0. \quad (12)$$

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