Acta Cryst. (1968). B**24**, 1121

The Crystal Structures of ThC₂

By Allen L. Bowman, N. H. Krikorian, George P. Arnold, Terry C. Wallace and Norris G. Nereson

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544, *U.S.A.*

(*Received* 28 *September* 1967)

A high-temperature neutron diffraction study of ThC_2 shows a cubic phase above 1480 °C and a tetragonal phase between 1430 and 1480°. The cubic phase has the KCN-type structure, $a_0=5{\cdot}80_6$ Å at 1550°, with randomly oriented C_2 groups. The structure of the tetragonal phase is derived from the cubic structure by compression along the *c* axis, with the C_2 groups randomly oriented in the plane perpendicular to the *c* axis. The body-centered cell parameters are $a_0=4{\cdot}221$, $c_0=5{\cdot}394$ Å at 1450 °C. The structure parameters of the C_g type monoclinic phase have been redetermined, giving a C–C distance of 1·32 Å, in close agreement with the values for other transition metal dicarbides.

The phase diagram of the thorium–carbon system (Wilhelm & Chiotti, 1950; Chiotti, Korbitz & Dooley, 1967) shows a compound, thorium dicarbide, of approximate composition ThC_2. The structure of this compound at room temperature has been described (Hunt & Rundle, 1951) as monoclinic, space group $C2/c$, with 4 thorium atoms in $(0,y,\frac{1}{4})$, $y=0{\cdot}202$ and 8 carbon atoms in (x,y,z), $x=0{\cdot}290$, $y=0{\cdot}132$, $z=0{\cdot}082$. Two high-temperature forms have been described recently from thermal analysis and high-temperature X-ray diffraction (Langer, Baldwin, Gantzel, Kester & Hancock, 1964; Hill & Cavin, 1964): a cubic form above 1480 °C, and a tetragonal form between 1430–1480°. The positions of the carbon atoms in these phases could not be determined.

Samples of thorium dicarbide containing excess carbon were prepared from the high-purity elements by arc-melting and pulverizing. A sample of nominal composition $ThC_{2.1}$ was examined by room-temperature neutron diffraction using a parallel-sided holder, made from a mull-matrix (Ti–Zr) alloy (Sidhu, Heaton, Zauberis & Campos, 1956). Diffraction data were obtained from $2\theta=5$ to 70° at a wavelength of 1·3366 Å. Chemical analysis of the sample showed Th 89·7%, C 9·38%, free C 0·23%, O 0·12%, N 270 ppm. The composition $ThC_{1{\cdot}97}$ obtained from the analysis is in excellent agreement with a recent determination of the phase boundary (Satow, 1967).

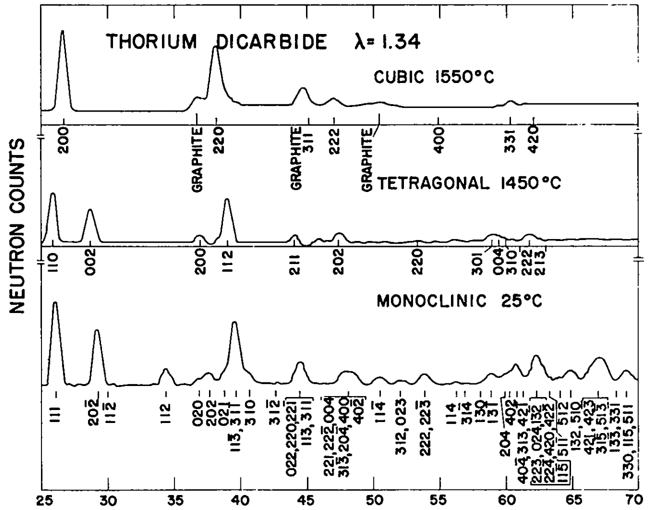

Fig. 1. Neutron diffraction powder pattern of thorium dicarbide.

A second sample of nominal composition $ThC_{2.25}$ was examined by thermal analysis (Rupert, 1965) and by high-temperature neutron diffraction (Bowman, Hull, Witteman, Arnold & Bowman, 1966). Diffraction patterns were obtained from $2\theta=15$ to 70° at 1150, 1450 and 1550 °C, and were corrected by subtracting a blank run on the graphite sample holder. The cubic form was observed at 1550°, the tetragonal form at 1450°, and the monoclinic form at 1150°. Thermal analysis showed two transformations at 1430 ± 20° and 1480 ± 20 °C. The pattern at 1150° was virtually identical with the room temperature pattern, and was not treated further. The corrected tetragonal pattern and the original cubic and monoclinic patterns are shown in Fig. 1. Chemical analysis after the diffraction experiments showed Th 89·6%, C 10·18%, free C 1·0%, O 550 ppm, N 200 ppm. Observed intensities were determined by least-squares analysis of the diffraction data (Bowman, Wallace, Yarnell, Wenzel & Storms, 1965), and were fitted to trial structures by least-squares solutions of the equation (Bacon, 1962)

$$I=K\frac{\exp(-\mu t\sec\theta)}{\sin^2 2\theta}\exp\left(-2B\frac{\sin^2\theta}{\lambda^2}\right)jF^2. \quad (1)$$

A composition $ThC_{1{\cdot}97}$ was used for the intensity calculations, with scattering factors of $1{\cdot}01\times10^{-12}$ cm for thorium and $0{\cdot}661\times10^{-12}$ cm for carbon.

The monoclinic structure previously reported was confirmed, with $K=0{\cdot}056\pm0{\cdot}001$, $B=0{\cdot}64\pm0{\cdot}08$, $y_{Th}=0{\cdot}2074\pm0{\cdot}0011$, $x_C=0{\cdot}2992\pm0{\cdot}0009$, $y_C=0{\cdot}1326\pm0{\cdot}0011$, $z_C=0{\cdot}0540\pm0{\cdot}0010$, $R=0{\cdot}04$, where $R=\Sigma\,w|I_o-I_c|/\Sigma\,wI_o$. Lattice parameters from the neutron diffraction pattern are $a_0=6{\cdot}692\pm0{\cdot}003$, $b_0=4{\cdot}223\pm0{\cdot}003$, $c_0=6{\cdot}744\pm0{\cdot}003$ Å, $\beta=103{\cdot}12\pm0{\cdot}11$°. The interatomic distances are listed in Table 1.

The intermediate phase is tetragonal, space group $I4/mmm$, with thorium atoms in (0,0,0) and C_2 groups centered in $(0,0,\frac{1}{2})$, randomly oriented in the plane per-

---

Work done under the auspices of the U.S. Atomic Energy Commission.

Table 1. *Interatomic distances in* ThC_2 (*monoclinic*)

Th–C	(2) $2{\cdot}44\pm0{\cdot}08$ A (2) $2{\cdot}66\pm0{\cdot}11$ (2) $2{\cdot}78\pm0{\cdot}11$ (2) $2{\cdot}90\pm0{\cdot}16$ (2) $2{\cdot}94\pm0{\cdot}07$ (2) $3{\cdot}76\pm0{\cdot}12$
Th–Th	(2) $3{\cdot}800\pm0{\cdot}005$ (4) $3{\cdot}957\pm0{\cdot}002$ (2) $4{\cdot}181\pm0{\cdot}008$ (1) $4{\cdot}19\pm0{\cdot}27$ (2) $4{\cdot}223\pm0{\cdot}003$ (1) $4{\cdot}39\pm0{\cdot}27$
C–C	(1) $1{\cdot}315\pm0{\cdot}041$

Table 2. *Neutron diffraction data for* $ThC_2(m)$

d	*hkl*	I_o	I_c
3·54	110	0·0	0·0
3·27	002	0·2	0·0
3·24	200	0·1	0·0
2·96	111	45·3	45·0
2·64	$20\bar{2}$	31·5	31·8
2·58	$11\bar{2}$	0·0	0·0
2·26	112	8·6	8·8
2·11	020	2·9	3·7
2·07	202	6·8	6·8
2·01	021	5·9	6·2
1·97	$11\bar{3}$ $31\bar{1}$	40·8	40·6
1·92	310	5·4	6·0
1·84	$31\bar{2}$	0·0	0·0
1·77	022 220 $22\bar{1}$ 113 311	16·1	15·8
1·64	221 $22\bar{2}$ 004 $31\bar{3}$ $20\bar{4}$ 400 $40\bar{2}$	14·6	14·8
1·57	$11\bar{4}$	4·9	4·6
1·52	312 023	2·8	3·0
1·48	222 $22\bar{3}$	7·0	7·1
1·42	114	0·9	1·4
1·40	$31\bar{4}$	0·0	0·0
1·38	130	0·2	0·6
1·36	$13\bar{1}$	6·5	7·3
1·34	204	5·1	3·7
1·33	402	1·0	3·4
1·32	$40\bar{4}$	10·8	8·4
1·31	313 $42\bar{1}$	0·1	2·0
1·29	223 024 $13\bar{2}$ $22\bar{4}$ 420 $42\bar{2}$ $11\bar{5}$	22·4	20·8
1·27	$51\bar{1}$	2·9	1·1
1·26	$51\bar{2}$	2·3	2·6
1·25	132 510	7·1	8·4

Table 2 (*cont.*)

d	*khl*	I_o	I_c
1·21	412 $42\bar{3}$ $31\bar{5}$ $51\bar{3}$	27·0	27·3
1·19	$13\bar{3}$ $33\bar{1}$	0·0	0·0
1·18	330 115 511	7·6	8·4

Table 3. *Neutron diffraction data for* $ThC_2(t)$

d	*hkl*	I_o	I_c
2·98	110	28·0	27·5
2·70	002	18·2	18·5
2·11	200	3·8	6·7
2·00	112	26·0	20·1
1·78	211	3·8	6·5
1·66	202	5·6	6·8
1·49	220	1·1	0·8
1·36	301	3·4	3·3
1·35	004	1·9	2·5
1·33	310	0·5	0·7
1·30	222 213	3·8	3·4

Table 4. *Neutron diffraction data for* $ThC_2(c)$

d	*hkl*	I_o	I_c
2·90	200	43·7	43·6
2·05	220	20·2	20·7
1·75	311	1·6	2·3
1·68	222	4·4	4·5
1·45	400	1·3	1·2
1·33	331	2·5	1·7
1·30	420	2·1	2·1

pendicular to the *c* axis, with $K=0{\cdot}14\pm0{\cdot}02$, $B=4{\cdot}0\pm1{\cdot}0$, $R=0{\cdot}12$, $d_{C-C}=1{\cdot}30\pm0{\cdot}02$ Å. The lattice parameters at 1450°C are $a_0=4{\cdot}221\pm0{\cdot}003$, $c_0=5{\cdot}394\pm0{\cdot}003$ Å.

The high-temperature phase is cubic, KCN-type (Elliott & Hastings, 1961; Sequeira, 1965), space group *Fm3m*, with thorium atoms in (0,0,0) and C_2 groups centered in $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The data were fitted with free rotating C_2 groups, with $K=0{\cdot}044\pm0{\cdot}002$, $B=7{\cdot}8\pm0{\cdot}5$, $R=0{\cdot}04$, $d_{C-C}=1{\cdot}24\pm0{\cdot}04$ Å. The alternate description of C_2 groups randomly aligned along [111] directions does not give a significantly different result. The lattice parameter at 1550° is $a_0=5{\cdot}806\pm0{\cdot}005$ Å.

The structures of the three thorium dicarbide phases are very closely related to each other. The high-temperature form is sodium chloride-type with C_2 groups randomly oriented in three dimensions so that cubic symmetry is maintained (KCN-type). As the temperature is lowered, the random orientation of the C_2 groups is reduced to two-dimensional in the tetragonal structure, and finally to a fixed alignment in the monoclinic structure. The metal lattice is distorted to maintain a closest packing about each different C_2 arrangement. The cubic structure is isomorphous with UC_2 (Bowman, Arnold, Witteman, Wallace & Nereson, 1966) and LaC_2 (Bowman, Krikorian, Arnold, Wallace

& Nereson, 1968). The tetragonal structure, however, is different from that of UC_2, LaC_2 and other known tetragonal dicarbides (Atoji, 1961) where the C_2 groups are aligned parallel to the *c* axis. The monoclinic structure is also unique among dicarbide structures.

The actual C–C distances in the high temperature phases are probably larger than the observed values, owing to the effect of thermal motion of the carbon atoms. Thus it would appear that the C–C distance is essentially constant at about 1·30–1·35 Å in all three phases, in good agreement with the other group 3A dicarbides.

References

Atoji, M. (1961). *J. Chem. Phys.* **35**, 1950.

Bacon, G. E. (1962). *Neutron Diffraction.* Oxford: Clarendon Press.

Bowman, A. L., Arnold, G. P., Witteman, W. G., Wallace, T. C. & Nereson, N. G. (1966). *Acta Cryst.* **21**, 670.

Bowman, A. L., Krikorian, N. H., Arnold, G. P., Wallace, T. C. & Nereson, N. G. (1968). *Acta Cryst.* **B24**, 459.

Bowman, A. L., Wallace, T. C., Yarnell, J. L., Wenzel, R. G. & Storms, E. K. (1965). *Acta Cryst.* **19**, 6.

Bowman, M. G., Hull, D. E., Witteman, W. G., Arnold, G. P. & Bowman, A. L. (1966). *Rev. Sci. Instrum.* **37**, 1543.

Chiotti, P., Korbitz, F. W. & Dooley, G. J., III (1967). *J. Nucl. Mat.* **23**, 55.

Elliott, N. & Hastings, J. (1961). *Acta Cryst.* **14**, 1018.

Hill, N. A. & Cavin, O. B. (1964). *J. Amer. Ceram. Soc.* **47**, 360.

Hunt, E. G. & Rundle, R. E. (1951). *J. Amer. Chem. Soc.* **73**, 4777.

Langer, S., Baldwin, N., Gantzel, P., Kester, F. & Hancock, C. (1964). *Nuclear Metallurgy, Vol.* X. *Compounds of Interest in Nuclear Reactor Technology*, p. 359. The Metallurgical Society of American Inst. of Mining, Metallurgical and Petroleum Engineers.

Rupert, G. N. (1965). *Rev. Sci. Instrum.* **36**, 1629.

Satow, T. (1967). *J. Nucl. Mat.* **21**, 249.

Sequeira, A. (1965). *Acta Cryst.* **18**, 291.

Sidhu, S. S., Heaton, L., Zauberis, D. D. & Campos, F. P. (1956). *J. Appl. Phys.* **27**, 1040.

Wilhelm, H. A. & Chiotti, P. (1950). *Trans. Amer. Soc. Metals*, **42**, 1295.

Acta Cryst. (1968). **B24**, 1123

The Crystal Structure of the Dimer of 9-Anthraldehyde

By Marianne Ehrenberg*

Department of Chemistry, University College, Gower Street, London W.C. 1, England

(*Received* 25 *October* 1967)

The structure of the dimer of 9-anthraldehyde has been determined by means of Patterson projections and three-dimensional least-squares refinements. The aldehyde groups are in the *trans* configuration.

Crystals of the dimer of 9-anthraldehyde, $[(C_{14}H_9)CHO]_2$, were prepared by P. Sarti-Fantoni, the dimerization taking place in the solid state by the action of ultraviolet radiation on the monomer. Studies of the infrared spectra (Craig & Sarti-Fantoni, 1966) indicated the *trans* configuration of the CHO groups with respect to the anthracene skeleton, although from the monomer structure a *cis* dimer formation might be expected. The structure determination was undertaken in order to confirm the *trans* configuration of the CHO groups with respect to the anthracene.

Crystal data

$a=9{\cdot}62$, $b=7{\cdot}86$, $c=8{\cdot}81$ Å $\alpha=59°40'$, $\beta=90°0'$, $\gamma=65°56'$
Density, measured $=1{\cdot}346$ g.cm^{-3}
Density, calculated $=1{\cdot}34$ g.cm^{-3}
Systematic absences: none
Space group $P\bar{1}$

Limited three-dimensional data were collected ($0kl \rightarrow 7kl, hk0$), the integrated intensities being read on a Joyce–Loebl flying-spot microdensitometer and corrected by the appropriate geometrical correction factors. The structure was solved from $h0l$ and $hk0$ Patterson projections and refined with the use of block-diagonal least-squares calculations on 640 observed reflexions. With isotropic temperature factors a discrepancy index of 10·9% was obtained; by using anisotropic temperature factors for the carbon and oxygen atoms, it was reduced to 8·8%. Table 1 gives the final positional and thermal parameters. The anisotropic temperature factors are not regarded as significant because of the paucity of the data.

The dimer molecules lie on centres of symmetry and hence the CHO groups must be in the *trans* configuration with respect to the anthracene skeleton. Bond lengths and angles have normal values within the accuracy of the structure determination. The bond length between C(9) and C(10′) connecting the two half-molecules is 1·61 Å, the same as found in dipara-anthracene (Ehrenberg, 1966*a*). Each half-molecule is bent through an angle of 2 × 23°, again similar to dipara-anthracene and the photo-isomer of bi(anthracene-9,10-dimethylene) (Ehrenberg, 1966*b*).

Fig. 1 is a schematic drawing of the molecule showing bond lengths and angles. The standard de-

---

* Present address: Sir John Cass College, Whitechapel High Street, London E.1, England.