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The Crystal and Molecular Structure of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin

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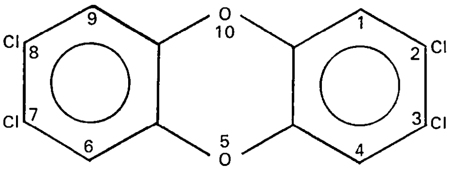
The crystal and molecular structure of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin has been determined by a three-dimensional single-crystal X-ray diffraction study. The lattice parameters of the triclinic unit cell: $a=3\cdot783\pm0\cdot003$, $b=9\cdot975\pm0\cdot009$, $c=15\cdot639\pm0\cdot015$ Å, $\alpha=94\cdot14\pm0\cdot02$, $\beta=95\cdot20\pm0\cdot04$, $\gamma=92\cdot77\pm0\cdot04°$, give a calculated density of 1·827 g.cm^{-3} for $C_{12}H_4O_2Cl_4$ and $Z=2$. The intensities of 2666 independent reflections were measured using the θ–2θ scan mode of a Picker four-circle diffractometer and Mo $K\alpha$ radiation. The space group $P\bar{1}$ was assigned on a statistical basis and subsequently confirmed by the excellent behavior of metric and thermal parameters upon refinement. The structure was solved from the Patterson function, and the coordinates of all atoms in the molecule, the isotropic temperature factors of the hydrogens, and the anisotropic temperature factors for the other atoms were refined by full-matrix least squares. The final R value was 3·6% for the 2381 reflections above background. The structure consists of two independent molecules situated on inversion centers at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and stacked along [100]. The molecules are essentially planar; no non-hydrogen atom deviates more than 0·018 Å from its least-squares molecular plane. Thus the approximate molecular symmetry is *mmm* (D_{2h}). The four unique C–Cl distances range from 1·726 to 1·730 Å, the four C–O distances from 1·377 to 1·379 Å, and the twelve C–C bonds are all between 1·374 and 1·388 Å. The C–O–C angles are 115·6 and 115·8°.

Introduction

The determination of the crystal structure of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin



is associated with a program to isolate chlorinated dioxins and to characterize their chemical and toxicological properties. The function of single-crystal X-ray diffraction is to identify positional isomers with certainty and thus establish the X-ray powder diffraction pattern (Boer, van Remoortere & Muelder, 1972) as an essentially unambiguous standard with which future samples can be compared. The literature contains one previous structure report of a chlorinated dibenzo-*p*-dioxin. Working under adverse experimental conditions, Cantrell, Webb & Mabis (1969) elucidated the crystal structure of 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin. In a conjoining study we report the crystal and molecular structure of 2,7-dichlorodibenzo-*p*-dioxin (Boer & North, 1972).

Methods of preparing 2,3,7,8-tetrachlorodibenzo-*p*-dioxin have been described previously (Tomita, Ueda & Narisada, 1959; Boer, van Remoortere & Muelder, 1972) and there is a considerable body of literature on its toxicological properties (Jones & Krizek, 1962; Schulz, 1968, Higginbotham, Huang, Firestone, Verrett, Ress & Campbell, 1968; Hegyi, St'ota & Luptakova, 1969; Sparschu, Dunn & Rowe, 1971).

Experimental

A crystalline sample of tetrachlorodibenzo-*p*-dioxin, originally prepared by chlorinating dibenzo-*p*-dioxin, was supplied by W. W. Muelder (Boer, van Remoortere & Muelder, 1972). The crystals, which were grown by sublimation, are colorless and of lathlike habit (elongated on **a** and with well developed $\{01\bar{1}\}$ faces). A crystal of dimensions 0·07 × 0·40 × 1·30 mm was selected for X-ray analysis and gently wedged into the tapered end of a 0·3 mm nominal internal diameter Lindemann glass capillary, which was immediately sealed. The precaution of enclosure in glass was taken to minimize the risk of accidentally exposing laboratory personnel. Surgical gloves were used in the crystal mounting operation, and the gloves and all mounting implements were subsequently incinerated.

The capillary was then attached to a conventional goniometer head with a putty-like substance. After the crystal had been aligned along **a** with oscillation photographs, the reciprocal lattice levels $0kl$ and $1kl$ were recorded on Weissenberg photographs. The crystal was then realigned along **a***, and precession photographs were taken of the $h0l$ and $hk0$ levels. The only reciprocal lattice symmetry observed was C_i indicating the crystal system to be triclinic (space group $P1$ or $P\bar{1}$). Interestingly, apparent systematic absences were observed for $0k0$, $k=2n+1$ and $00l$, $l=2n+1$, and the $0kl$ Weissenberg level showed approximate mirror planes across the b^* and c^* axes. The significance of these features will be discussed in a later section. After this preliminary survey, the crystal was carefully centered on a Picker four-circle goniostat and the alignment along **a*** was refined. Lattice constants were determined by least-squares refinement of the setting angles of 17 reflections with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). The crystal data are listed in Table 1, with the errors increased by a factor of ten from those obtained from the least-squares refinement, reflecting our experience with systematic instrumental errors and reproducibility of results under different experimental conditions. Space group $P1$, with two molecules per unit cell, requires the presence of two independent molecules in general positions, while $P\bar{1}$ permits either one molecule in a general position or two located on separate inversion centers.

Table 1. *Crystal data*

Molecular formula		$C_{12}H_4O_2Cl_4$
Molecular weight		321·977
Crystal habit		Lath
Space group		$P\bar{1}$ (No. 2, C_i^1)
Cell constants	a	3·783 ± 0·003 Å
(reduced cell)	b	9·975 ± 0·009
25 °C	c	15·639 ± 0·015
	α	94·14 ± 0·02°
	β	95·20 ± 0·04
	γ	92·77 ± 0·04
Volume	V	585·3 ± 0·4 Å^3
Density	$\varrho_{(calc)}$	1·827 g.cm^{-3} ($Z=2$)
Absorption coefficient μ(Mo $K\alpha$)		9·793 cm^{-1}
Number of independent reflections observed		2666

The θ–2θ scan mode of the Picker diffractometer and Mo $K\alpha$ radiation, monochromated with the 002 reflection of a highly oriented graphite crystal, were used to obtain the intensity data. The X-ray tube was at a 3·0° take-off angle, and the scintillation detector was 31·6 cm from the crystal and screened with a 4 mm square aperture. Incident- and exit-beam collimators 1·5 mm in diameter were used to restrict stray radiation. Attenuators were employed to prevent the count rate from exceeding 12,000/sec. The scan speed was 2°/min over 2θ angles of $2{\cdot}0° + \Delta$, where Δ is the separation of the $K\alpha$ doublet; this range was sufficient to allow for the observed mosaic spread of the crystal. Stationary-crystal stationary-counter background counts of 10 sec were taken at each end of the scan. A sphere $0 < \sin\,\theta \le 0{\cdot}46$, equivalent to the Cu $K\alpha$ sphere, was examined. The 033 reflection was monitored after every 50 measurements and showed good stability, as indicated by a root-mean-square deviation of less than 1% in intensity and a maximum deviation of 2·8%. An error $\sigma(I) = [(0{\cdot}02I)^2 + N_o + k^2N_b]^{1/2}$ was assigned to the net intensity $I = N_o - kN_b$ of each reflection in order to establish the weights $w(F) = 4F^2/\sigma^2(F^2)$ for subsequent least-squares refinement, where the quantity $\sum w(|F_o| - |F_c|)^2$ was minimized. Here N_o is the gross count, N_b is the background count, k is the ratio of scan time to background time, and the F^2 are the intensities corrected for Lorentz and polarization effects *via* the expression $\text{Lp}^{-1} = \sin 2\theta(1 + \cos^2 2\theta_m)/(1 + \cos^2 2\theta \cos^2 2\theta_m)$, where $2\theta_m$ is the monochromator setting angle. The 285 reflections for which $I < 0$ or $I/\sigma(I) < 2{\cdot}0$ were denoted absent and were not used in the refinement. The intensity data were corrected for absorption (de Meulenaer & Tompa, 1965); transmission factors ranged from a minimum of 0·692 to a maximum of 0·932.

An overall temperature factor ($B_o = 3{\cdot}275$ Å^2) was calculated by Wilson's (1942) method. The distribution

Table 2. *Final structure parameters with standard deviations in parentheses*

The anisotropic thermal parameters are in the form $\exp -(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$.

(*a*) Heavy atoms (anisotropic thermal parameters)

	$x(\times 10^5)$	$y(\times 10^5)$	$z(\times 10^5)$	$10^4\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Cl(2*A*)	24332 (15)	−28365 (5)	26900 (3)	758 (5)	865 (6)	301 (2)	325 (13)	−130 (8)	132 (3)
Cl(3*A*)	−17456 (16)	−47674 (5)	11985 (4)	841 (5)	617 (5)	407 (2)	−179 (13)	152 (9)	78 (3)
Cl(2*B*)	10613 (16)	77903 (6)	77142 (3)	803 (5)	924 (6)	310 (2)	455 (14)	463 (8)	95 (3)
Cl(3*B*)	17045 (17)	97910 (6)	62508 (4)	864 (5)	635 (5)	469 (3)	645 (13)	340 (10)	48 (3)
O(*A*)	19947 (40)	08571 (14)	06607 (9)	800 (13)	629 (15)	248 (6)	386 (35)	−217 (22)	16 (7)
O(*B*)	46780 (42)	40986 (13)	56599 (9)	920 (14)	620 (15)	244 (6)	682 (36)	359 (23)	56 (7)
C(1*A*)	20316 (53)	−9398 (20)	15576 (13)	465 (14)	678 (21)	256 (8)	220 (43)	8 (27)	−25 (10)
C(2*A*)	11584 (51)	−22616 (20)	16989 (12)	464 (14)	723 (21)	255 (8)	435 (43)	98 (27)	76 (10)
C(3*A*)	−6777 (52)	−31053 (19)	10454 (13)	472 (14)	545 (19)	325 (9)	108 (42)	231 (28)	36 (10)
C(4*A*)	−17010 (53)	−26211 (20)	02588 (13)	463 (14)	635 (20)	276 (9)	3 (42)	79 (27)	−43 (10)
C(5*A*)	−8608 (50)	−13010 (19)	01266 (12)	437 (14)	656 (20)	225 (8)	116 (41)	87 (25)	12 (9)
C(6*A*)	10264 (50)	−4631 (19)	07732 (12)	453 (14)	587 (19)	253 (8)	119 (41)	126 (26)	−6 (10)
C(1*B*)	29579 (55)	58979 (21)	65628 (13)	529 (16)	731 (22)	256 (8)	168 (46)	148 (28)	8 (11)
C(2*B*)	22673 (51)	72370 (21)	67145 (13)	446 (14)	762 (22)	261 (8)	161 (44)	122 (27)	−74 (10)
C(3*B*)	25627 (52)	81109 (20)	60742 (13)	452 (15)	594 (20)	346 (9)	265 (42)	5 (29)	44 (11)
C(4*B*)	35698 (56)	76516 (21)	52812 (13)	556 (16)	648 (21)	305 (9)	226 (45)	113 (29)	51 (11)
C(5*B*)	42831 (50)	63162 (20)	51347 (12)	446 (14)	665 (20)	236 (8)	272 (41)	68 (26)	5 (10)
C(6*B*)	39708 (52)	54373 (19)	57761 (12)	473 (14)	604 (20)	267 (8)	242 (41)	35 (27)	5 (10)

(*b*) Hydrogen atoms (isotropic thermal parameters)

	$x(\times 10^4)$	$y(\times 10^4)$	$z(\times 10^4)$	B
H(1*A*)	3493 (57)	−369 (23)	1996 (14)	3·6 (5)
H(4*A*)	−3102 (52)	−3208 (20)	−219 (13)	2·3 (4)
H(1*B*)	2730 (53)	5287 (21)	7043 (13)	2·9 (4)
H(4*B*)	3803 (53)	8316 (21)	4815 (13)	2·7 (4)

Table 3. *Observed and calculated structure factors in* $e \times 10$

H	K	FOBS	FCAL
** L = 0 **			
1	0	491	498
2	0	377	379
3	0	253	261
4	0	47	44
1	-1	229	220
1	1	997	1010
2	1	44	38
2	-1	111	101
3	1	94	92
4	1	22	21
4	-1	30	28
0	2	130	128
1	-2	150	140
1	2	71	69
2	2	162	151
2	-2	151	145
3	-2	155	149
3	2	55	53
4	2	37	34
4	-2	30	27
0	3	24	23
1	-3	274	263
1	3	361	360
2	3	162	161
2	-3	98	93
3	-3	34	32
3	3	22	28
4	3	33	27
4	-3	63	61
0	4	605	622
1	-4	274	256
1	4	378	375
2	4	147	146
2	-4	297	285
3	-4	33	34
3	4	198	202
4	4	102	101
4	-4	24	25
0	5	16	14
1	-5	336	310
1	5	88	91
2	5	214	212
2	-5	67	65
3	-5	62	60
3	5	63	89
4	5	20	12
4	-5	114	112
0	6	155	140
1	-6	147	141
1	6	260	262
2	6	245	248
2	-6	270	271
3	-6	183	181
3	6	119	118
1	-7	77	77
1	7	84	84
2	7	69	67
2	-7	84	86
3	7	31	33
4	-7	95	93
0	8	81	80
1	-8	144	152
1	8	210	214
2	8	59	59
2	-8	89	91
3	-8	88	92
3	8	158	155
0	9	20	10
1	-9	83	88
1	9	23	20
2	9	34	29
2	-9	96	100
3	-9	80	82
3	9	64	63
0	10	95	98
1	-10	90	86
1	10	174	127
2	10	65	65
2	-10	205	212
3	-10	75	71
1	-11	118	121
1	11	21	0
2	11	79	74
2	-11	130	135
0	12	58	60
1	-12	140	142
1	12	66	65
2	-12	53	45
** L = 1 **			
0	0	15	17
-1	0	354	347
1	0	945	959
2	0	145	149
-2	0	210	214
-3	0	196	202
3	0	35	31
4	0	45	44
-4	0	30	31
0	1	160	163
0	-1	162	160
1	-1	93	87
-1	1	264	249
1	1	834	836
-1	-1	439	423
-2	-1	194	190
2	1	79	79
-2	1	46	41
2	-1	246	231
3	-1	51	45
-3	1	51	53
3	1	52	52
-3	-1	86	83
-4	-1	45	41
4	1	61	58
-4	1	30	28
4	-1	46	44
0	-2	244	245
0	2	241	244
-1	2	426	417
1	-2	315	307
1	2	160	162
-1	-2	148	150
2	2	119	114
-2	-2	158	156
2	-2	111	107
-2	2	55	50
-3	2	164	166
3	-2	160	159
-3	-2	99	98
3	2	21	17
4	2	48	49
-4	-2	80	77
4	-2	22	13
-4	2	95	96
0	3	262	261
0	-3	294	298
1	-3	335	329
-1	3	219	217
1	3	270	267
-1	-3	91	89
-2	-3	75	74
2	3	87	89
-2	3	279	277
2	-3	16	10
3	-3	215	214
-3	3	89	87
3	3	74	72
-3	-3	115	117
-4	-3	55	54
-4	3	21	20
4	-3	34	31
0	-4	224	219
0	4	240	239
-1	4	225	211
1	-4	74	77
-1	-4	280	278
1	4	195	190
2	4	135	135
-2	-4	143	144
2	-4	400	390
-2	4	103	105
-3	4	23	19
3	-4	91	92
-3	-4	136	136
3	4	42	44
4	4	32	25
-4	-4	36	31
4	-4	78	79
-4	4	55	48
0	5	511	504
0	-5	686	675
1	-5	446	439
-1	5	181	185
-1	-5	425	418
-2	-5	58	58
2	5	46	46
-2	5	28	24
2	-5	191	194
3	-5	31	30
-3	5	71	70
3	5	69	68
-3	-5	198	200
-4	-5	38	35
4	5	66	65
-4	5	21	14
4	-5	85	87
0	-6	342	352
0	6	375	385
-1	6	484	479
1	-6	118	123
1	6	22	15
2	6	354	357
-2	-6	45	43
2	-6	58	60
-3	6	122	125
3	-6	104	111
-3	-6	53	57
3	6	117	115
4	6	35	33
-4	-6	53	51
4	-6	48	44
-4	6	25	15
0	7	144	144
0	-7	175	175
1	-7	77	75
-1	7	168	170
1	7	142	145
-1	-7	101	102
-2	-7	50	49
-2	7	178	184
2	-7	78	77
3	-7	61	56
-3	7	82	81
3	7	76	76
-3	-7	59	56
-4	7	31	28
4	-7	49	44
0	-8	40	37
0	8	28	19
-1	8	65	65
1	-8	88	89
-1	-8	25	11
1	8	59	60
2	8	27	29
-2	-8	130	130
2	-8	50	50
-2	8	39	45
3	-8	90	89
3	8	42	38
0	9	27	26
1	-9	178	175
-1	9	17	20
-1	-9	178	180
-2	-9	39	36
2	-9	109	107
3	-9	37	37
-3	9	40	40
3	9	23	12
-3	-9	32	27
0	-10	155	155
0	10	182	181
-1	10	128	132
1	-10	30	25
1	10	32	31
-1	-10	106	107
2	10	101	99
-2	-10	61	57
2	-10	46	43
-2	10	57	61
-3	10	51	59
0	11	21	16
0	-11	47	49
-1	11	77	76
1	11	146	141
-1	-11	49	50
-2	-11	26	30
2	11	114	111
-2	11	67	67
2	-11	46	40
0	-12	48	48
0	12	58	54
-1	12	29	22
1	-12	41	38
1	12	54	46
2	-12	46	38
-2	12	38	35
** L = 2 **			
0	0	10	5
-1	0	122	114
1	0	664	671
2	0	239	239
-2	0	137	133
-3	0	26	20
3	0	40	45
4	0	25	21
-4	0	70	75
0	1	405	423
0	-1	422	438
1	-1	70	64
-1	1	1432	1382
1	1	693	710
-1	-1	41	40
-2	-1	43	38
2	1	808	831
-2	1	521	526
2	-1	91	91
3	-1	38	31
-3	1	50	55
3	1	69	77
-3	-1	17	5
-4	-1	60	60
-4	1	53	56
4	1	65	70
4	-1	100	93
0	-2	492	505
0	2	473	495
-1	2	323	313
1	-2	139	126
1	2	20	21
-1	-2	353	347
2	2	152	151
-2	-2	119	113
2	-2	63	53
-2	2	102	100
-3	2	44	42
3	-2	28	5
-3	-2	72	67
3	2	219	223
4	2	19	23
-4	-2	26	15
0	3	141	138
0	-3	199	197
1	-3	505	501
-1	3	200	198
1	3	114	110
-1	-3	409	408
-2	-3	531	527
2	3	16	16
-2	3	79	79
2	-3	154	145
-3	3	76	79
3	-3	26	23
3	3	30	26
-4	-3	87	88
-4	3	225	224
4	-3	55	53
0	-4	348	345
0	4	372	367
-1	4	87	75
1	-4	37	33
-1	-4	382	370
1	4	77	78
2	4	187	191
-2	-4	76	73
2	-4	212	200
-2	4	25	27
-3	4	87	88
3	-4	73	70
-3	-4	205	202
3	4	86	86
4	4	26	16
-4	-4	55	49
-4	4	51	51
4	-4	39	37
0	5	298	289
0	-5	288	275
1	-5	382	372
-1	5	296	291
1	5	468	476
-1	-5	216	205
2	5	293	295
-2	-5	26	28
-2	5	23	18
3	-5	50	49
-3	5	88	90
3	5	32	22
-3	-5	126	127
4	5	96	50
-4	-5	115	121
4	-5	87	86
0	-6	59	61
0	6	15	18
-1	6	121	117
1	-6	30	27
-1	-6	104	109
1	6	281	278
2	6	38	35
-2	-6	39	37
2	-6	48	48
-2	6	27	24
-3	6	71	71
3	-6	96	97
-3	-6	72	71
3	6	42	32
4	-6	32	26
-4	6	22	18
0	-7	308	314
0	7	258	263
1	-7	141	136
-1	7	164	172
-1	-7	149	149
1	7	202	206
-2	-7	246	248
2	7	110	110
2	-7	61	65
-2	7	56	60
3	-7	46	46
-3	7	135	137
3	7	76	76
-3	-7	57	58
-4	7	111	109
0	-8	49	51
0	8	24	27
-1	8	71	76
-1	-8	141	139
1	8	28	29
2	8	74	76
-2	-8	103	100
2	-8	105	104
-2	8	122	126
-3	8	68	64
3	-8	93	92
-3	-8	48	46
3	8	44	43
0	9	175	179
0	-9	190	196
1	-9	213	215
-2	-9	45	39
2	9	140	139
-2	9	58	58
3	-9	142	142
-3	9	76	78
3	9	48	46
-3	-9	105	106
0	10	68	75
0	-10	68	76
1	-10	104	109
-1	10	25	19
-1	-10	32	28
2	10	21	12
-2	-10	25	10
2	-10	66	66
-2	10	61	61
-3	10	51	42
3	-10	130	136
0	11	138	144
0	-11	134	142
1	-11	28	23
-1	11	155	156
1	11	24	4
-1	-11	55	55
-2	-11	56	59
2	11	54	53
2	-11	75	80
0	-12	43	45
0	12	49	51
-1	12	40	37
1	-12	23	9
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1	12	47	41
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2	-2	16	6
-2	2	31	21
-3	2	19	17
3	-2	42	38
-3	-2	24	23
0	3	136	140
0	-3	109	112
1	-3	41	76
-1	3	104	108
1	3	104	101
-1	-3	103	101
-2	-3	85	86
2	3	37	34
2	-3	59	61
-2	3	49	21
-3	3	61	63
3	-3	68	64
-3	-3	32	25
0	-4	72	80
0	4	47	74
1	-4	19	15
-1	-4	129	130
1	4	114	112
2	4	69	65
-2	-4	24	16
-3	-4	88	85
0	-5	125	124
0	5	63	62
1	-5	22	14
-1	5	130	125
-1	-5	65	67
-2	-5	38	33
2	5	113	108
-2	5	87	86
2	-5	47	39
-3	5	28	24
-3	-5	68	62
0	6	70	75
0	-6	102	105
-1	6	67	62
1	-6	47	53
-1	-6	32	25
1	6	77	76
-2	-6	88	85
2	-6	42	38

Table 3 (*cont.*)

H	K	FOBS	FCAL
-2	6	30	35
-3	-6	26	26
0	7	109	107
0	-7	113	119
1	-7	59	57
-1	7	126	121
1	7	38	33
-1	-7	59	56
-2	-7	45	45
-2	7	55	52
2	-7	26	26
-1	8	41	38
-1	-8	24	18
-2	-8	42	36
2	-8	34	29
0	-9	49	41
1	-9	31	27
-1	-9	69	69
** L = 15 **			
1	0	88	89
-2	0	48	50
2	0	172	171
-3	0	22	11
0	1	31	24
-1	1	64	62
1	-1	127	130
-1	-1	17	6
1	1	20	16
2	1	23	12
-2	1	67	64
2	-1	162	158
-3	-1	45	43
-3	1	94	95
0	-2	123	125
0	2	81	85
-1	2	272	268
1	-2	93	94
-1	-2	90	89
1	2	60	62
2	2	67	63
-2	-2	138	138
2	-2	34	37
-2	2	225	233
-3	-2	23	21
0	-3	30	21
1	-3	47	43
-1	3	155	160
-1	-3	135	135
1	3	41	39
2	-3	71	71
-2	3	40	34
-3	3	49	52
-3	-3	114	111
0	-4	113	117
0	4	79	81
1	-4	197	205
-1	4	40	41
-1	-4	18	7
1	4	47	48
2	4	32	34
-2	-4	101	98
2	-4	66	64
-2	4	89	88
-3	4	53	50
-3	-4	70	72
0	5	152	148
0	-5	124	126
1	-5	27	24
-1	5	85	83
-1	-5	82	79
-2	-5	31	31
2	5	19	7
-2	5	58	53
2	-5	90	88
-3	-5	41	37
0	-6	26	21
-1	6	143	140
1	-6	25	14
1	6	100	95
-1	-6	25	31
-2	-6	35	32
2	-6	69	72
-2	6	136	133
0	7	40	39
0	-7	74	73
1	-7	53	57
-1	7	70	64
1	7	21	7
-1	-7	33	28
-2	-7	25	26
-2	7	36	25
2	-7	66	62
0	-8	117	112
1	-8	141	141
-1	-8	55	52
0	-9	69	65
-1	-9	117	110
** L = 16 **			
-1	0	96	94
1	0	102	101
-2	0	40	37
0	-1	95	95
0	1	89	94
-1	1	90	88
1	-1	112	112
-1	-1	111	115
1	1	18	1
-2	-1	19	16
2	1	56	53
-2	1	22	7
0	-2	188	183
0	2	184	182
-1	2	122	124
1	-2	20	17
1	2	98	97
2	2	39	34
-2	-2	107	104
2	-2	64	56
-3	2	74	74
-3	-2	72	68
0	-3	46	44
0	3	35	26
1	3	60	58
-2	-3	32	31
2	3	29	31
2	-3	33	26
-2	3	25	8
-3	3	36	29
0	-4	42	43
0	4	21	6
1	-4	59	58
-1	-4	131	128
-2	-4	69	72
2	-4	23	17
-2	4	75	65
-3	-4	33	33
0	5	31	32
0	-5	42	37
1	-5	68	70
-1	-5	125	122
-2	-5	24	20
-2	5	23	12
2	-5	23	29
0	6	96	90
0	-6	84	80
-1	6	39	39
1	-6	27	17
-1	-6	49	43
1	6	92	87
-2	-6	49	45
2	-6	118	117
-2	6	37	35
0	-7	25	23
1	-7	32	28
-1	7	71	67
-1	-7	54	47
-2	-7	24	14
0	-8	24	27
1	-8	54	48
-1	-8	44	35
** L = 17 **			
1	0	64	58
2	0	30	26
-2	0	70	67
0	-1	52	50
0	1	36	29
-1	1	22	10
1	-1	19	18
-1	-1	81	78
1	1	41	39
-2	-1	21	22
2	1	53	51
-3	-1	124	118
0	2	41	43
-1	2	48	44
1	-2	18	15
-1	-2	65	61
1	2	26	20
-2	-2	124	121
2	-2	99	96
-2	2	94	91
0	-3	127	131
0	3	145	147
-1	3	49	40
1	3	54	51
-1	-3	83	84
-2	-3	38	35
-2	3	125	125
2	-3	76	77
0	-4	97	94
0	4	78	75
-1	4	33	41
1	-4	115	115
-1	-4	72	70
1	4	70	68
2	-4	21	22
-2	4	110	106
0	-5	22	28
0	5	29	32
1	-5	19	8
-1	5	74	71
1	5	26	25
-2	-5	53	49
-2	5	27	27
0	6	22	24
0	-6	28	17
1	-6	77	76
-1	6	84	78
-1	-6	50	51
-2	-6	26	23
0	-7	105	102
1	-7	46	44
-1	-7	114	107
** L = 18 **			
0	0	109	107
1	0	96	97
-2	0	75	70
0	1	85	85
0	-1	48	50
-1	1	49	45
1	-1	119	110
-1	-1	136	132
-2	-1	86	80
-2	1	25	14
0	-2	71	68
0	2	60	57
1	-2	89	84
1	2	75	72
-2	-2	25	19
-2	2	31	28
0	-3	70	69
1	-3	33	28
-1	3	144	141
1	3	112	105
-1	-3	95	98
-2	3	145	139
0	-4	49	53
0	4	25	27
1	-4	61	59
-1	4	30	31
-1	-4	31	24
-2	-4	77	75
1	-5	86	74
-1	-5	45	41
0	-6	22	23
-1	-6	27	26
** L = 19 **			
-1	0	81	74
-2	0	65	65
-1	1	26	25
1	-1	45	39
-1	-1	67	60
-2	-1	61	52
-2	1	30	21
0	-2	26	29
0	2	32	20
1	-2	51	54
-1	-2	35	29
-2	-2	44	39
0	3	60	56
0	-3	38	37
-1	3	63	63
-1	-3	31	24
0	-4	39	43
0	-5	75	71
-1	-5	35	20
** L = 20 **			
0	0	156	144
0	-1	71	69
-1	-1	107	95
0	-2	38	38
-1	-2	40	42

of intensities was very close to the theoretical distribution for centric space groups.

Solution and refinement of the structure

The intensity statistics, taken together with the pseudo-orthogonal symmetry about the b^* and c^* axes and the pseudoabsences on the $0kl$ reciprocal lattice level, allowed us to form some hypotheses concerning the crystal structure: (1) the space group was $P\bar{1}$, (2) the structure approximates the rectangular two-dimensional space group pgg in a-axis projection, and therefore (3) two independent molecules are present in the cell on inversion centers related by $x=0$ or $\frac{1}{2}$, $y=\frac{1}{2}$, and $z=\frac{1}{2}$. These assumptions proved to be correct and are evident in the final structure as drawn in Figs. 1 and 2. A somewhat similar case has previously been described by Rabinovich & Schmidt (1964): 2,5-dimethyl-1,4-benzoquinone crystallizes in space group $P\bar{1}$ $(Z=2)$ with two molecules related by a pseudo-n-glide at the centers of symmetry (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. In our case, however, pseudo-absences do not appear in the upper reciprocal lattice levels and the pseudosymmetry applies only to the projection.

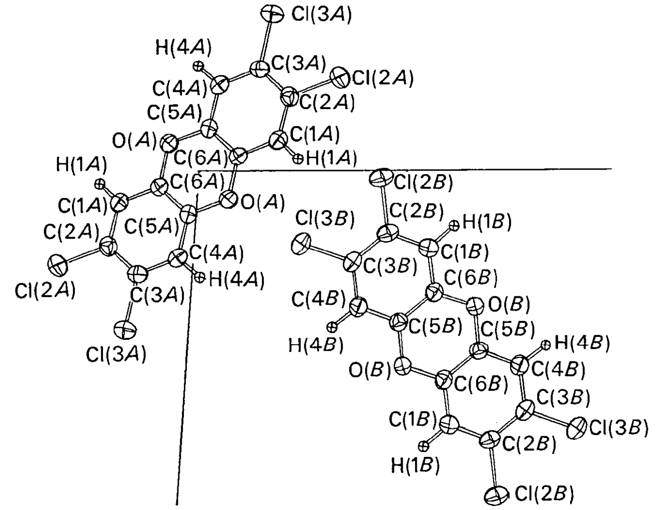

Fig. 1. The two independent molecules in the crystal structure of 2,3,7,8-tetrachlorodibenzo-p-dioxin. The molecules are centered at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and the y (vertical) and z (horizontal) axes are drawn.

The structure was solved from a normal-sharpened three-dimensional Patterson function by recognition of the intramolecular vector interactions Cl(2*A*) → Cl(3*A*) and Cl(2*A*) → Cl(3*A'*) at (0·40, 0·19, 0·30) and (0·05, −0·75, 0·78) respectively. (Primes designate transformations through the inversion centers.) A planar model of a 2,3,7,8-tetrachlorodibenzo-p-dioxin molecule calculated from standard bond distances and angles (Sutton, 1965) and including the hydrogen atoms, was generated and oriented about the origin using these vectors. A structure factor calculation gave $R_1=\sum||F_o|-|F_c||/\sum|F_o|=0\cdot575$ and $R_2=\{\sum w(F_o-F_c)^2/\sum wF_o^2\}^{1/2}=0\cdot857$, and an electron density map calculated with the resulting phases showed the second molecule (B) about the inversion center at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Using the Cl positions of molecule B to generate reference vectors, we then oriented our mathematical model of the molecule about this second center and proceeded with refinement.

The structure was refined by full-matrix least-squares with the inclusion of anomalous scattering factors for chlorine. In successive cycles, the positions of the non-hydrogen atoms, their isotropic temperature factors, the hydrogen positions, and finally the hydrogen isotropic temperature factors were introduced as varied parameters. The initial R values were $R_1=0\cdot296$ and $R_2=0\cdot380$; when convergence had been attained these values were reduced to 0·120 and 0·138 respectively.

At this stage we endeavored to test the possibility that the structure might be refined in the non-centric space group $P1$. As a precaution, the atomic positions were first given random shifts. At convergence, the R values had in fact been reduced by about 10%. From this result alone, one might conclude that the $P1$ model is to be preferred at a high probability level – the ratio R_2(centric)/R_2(acentric) of 1·113 is well in excess of $\mathscr{R}_{85,2207,0\cdot005}=1\cdot0256$ interpolated from Hamilton's (1965) significance test tables. However, inspection of the metric parameters of the refined $P1$ and $P\bar{1}$ structures shows that the standard deviations (σ) from the average values for chemically related distances and angles are 5 to 10 times greater in the acentric space group. Thermal parameters also showed a wider variation in $P1$, particularly for the hydrogen atoms, some of which assumed negative temperature factors. Most of the deviations exhibited by the $P1$ model seem to be meaningless from a structural standpoint, whereas the distances, angles, and temperature factors of the $P\bar{1}$ model are all well-behaved. Accordingly, we must conclude that the centric model appears to be satisfactory, and that additional refinement in $P1$ would be fruitless in view of the poorly conditioned normal equations encountered.

The introduction of anisotropic thermal parameters for the Cl, C, and O atoms gave a sharp drop in the R values, which were reduced to $R_1=0·040$ and $R_2=0·042$ after one cycle. A correction was now made for secondary extinction (Zachariasen, 1963). The maximum change in F_{meas} was 8% for $1\bar{1}\bar{2}$. After three additional cycles in which all positional parameters, non-hydrogen anisotropic thermal parameters and hydrogen isotropic temperature factors were varied, the final values $R_1=0·036$ and $R_2=0·038$ (for the 2381 reflections above background) were reached. In the final cycle, no parameter shift exceeded $0·02\sigma$. The largest positive peak in the final difference Fourier had an amplitude of 0·33 e.Å^{-3} while the largest negative peak, which appeared at the centroid of molecule B at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ was $-0·25$ e.Å^{-3}.

Final atomic parameters and their standard deviations as calculated in the last cycle of least-squares refinement are given in Table 2. Table 3 lists observed and calculated structure factors. Intramolecular distances and angles with standard deviations obtained from the least-squares variance–covariance matrix are presented in Table 4. The two independent molecules in the crystal structure are shown in three dimensions in Fig. 1 where the thermal ellipsoids are drawn at 50% probability.

The atomic scattering factors for Cl, C, and O were taken from *International Tables for X-ray Crystallography* (1962). The scattering factor for hydrogen is that given by Stewart, Davidson & Simpson (1965). Fourier summations, least-squares refinements, and error analysis were based on adaptations of standard programs by Gvildys (1964, 1965, 1967) and illustrations were prepared using our own adaptation of the thermal ellipsoid plot program of Johnson (1965).

Table 4. *Bond distances and angles in* 2,3,7,8-*tetrachlorodibenzo-p-dioxin*

Standard errors calculated from the variance–covariance matrix obtained in the final least-squares cycle are given in parentheses. Primes designate atoms related by the inversion centers in the molecules.

Distances

Cl(2*A*)–C(2*A*)	1·727 (2) Å	Cl(2*B*)–C(2*B*)	1·728 (2) Å
Cl(3*A*)–C(3*A*)	1·726 (3)	Cl(3*B*)–C(3*B*)	1·730 (3)
O(*A*)—C(3*A*)	1·378 (3)	O(*B*)—C(6*B*)	1·377 (3)
O(*A*)—C(5*A′*)	1·378 (3)	O(*B*)—C(5*B′*)	1·379 (3)
C(1*A*)–C(2*A*)	1·382 (3)	C(1*B*)–C(2*B*)	1·381 (3)
C(2*A*)–C(3*A*)	1·388 (3)	C(2*B*)–C(3*B*)	1·383 (3)
C(3*A*)–C(4*A*)	1·384 (3)	C(3*B*)–C(4*B*)	1·383 (3)
C(4*A*)–C(5*A*)	1·374 (3)	C(4*B*)–C(5*B*)	1·379 (3)
C(5*A*)–C(6*A*)	1·386 (3)	C(5*B*)–C(6*B*)	1·388 (3)
C(6*A*)–C(1*A*)	1·376 (3)	C(6*B*)–C(1*B*)	1·376 (3)
C(1*A*)–H(1*A*)	0·97 (2)	C(1*B*)–H(1*B*)	1·01 (2)
C(4*A*)–H(4*A*)	1·01 (2)	C(4*B*)–H(4*B*)	1·03 (2)

Table 4 (*cont.*)

Angles

Vertex	Atom 1	Atom 2		Vertex	Atom 1	Atom 2	
O(*A*)	C(6*A*)	C(5*A′*)	115·56 (15)°	O(*B*)	C(6*B*)	C(5*B′*)	115·78 (15)°
C(1*A*)	C(2*A*)	C(6*A*)	119·72 (18)	C(1*B*)	C(2*B*)	C(6*B*)	119·90 (19)
	C(2*A*)	H(1*A*)	120·0 (1·3)		C(2*B*)	H(1*B*)	118·2 (1·2)
	C(6*A*)	H(1*A*)	120·1 (1·3)		C(6*B*)	H(1*B*)	121·9 (1·2)
C(2*A*)	C(1*A*)	C(3*A*)	119·86 (19)	C(2*B*)	C(1*B*)	C(3*B*)	120·07 (19)
	C(1*A*)	Cl(2*A*)	118·92 (16)		C(1*B*)	Cl(2*B*)	118·81 (16)
	C(3*A*)	Cl(2*A*)	121·21 (17)		C(3*B*)	Cl(2*B*)	121·12 (17)
C(3*A*)	C(2*A*)	C(4*A*)	120·27 (19)	C(3*B*)	C(2*B*)	C(4*B*)	120·25 (19)
	C(2*A*)	Cl(3*A*)	120·87 (17)		C(2*B*)	Cl(3*B*)	120·78 (16)
	C(4*A*)	Cl(3*A*)	118·86 (16)		C(4*B*)	Cl(3*B*)	118·97 (16)
C(4*A*)	C(3*A*)	C(5*A*)	119·52 (18)	C(4*B*)	C(3*B*)	C(5*B*)	119·50 (19)
	C(3*A*)	H(4*A*)	121·7 (1·2)		C(3*B*)	H(4*B*)	119·3 (1·2)
	C(5*A*)	H(4*A*)	118·8 (1·2)		C(5*B*)	H(4*B*)	121·2 (1·2)
C(5*A*)	C(4*A*)	C(6*A*)	120·30 (19)	C(5*B*)	C(4*B*)	C(6*B*)	120·27 (19)
	C(4*A*)	O(*A′*)	117·46 (16)		C(4*B*)	O(*B′*)	117·75 (18)
	C(6*A*)	O(*A′*)	122·24 (18)		C(6*B*)	O(*B′*)	121·98 (18)
C(6*A*)	C(5*A*)	C(1*A*)	120·31 (19)	C(6*B*)	C(5*B*)	C(1*B*)	120·02 (19)
	C(5*A*)	O(*A*)	122·17 (18)		C(5*B*)	O(*B*)	122·24 (18)
	C(1*A*)	O(*A*)	117·52 (17)		C(1*B*)	O(*B*)	117·74 (18)

Discussion

The crystal structure (Fig. 2) contains two independent molecular stacks, A and B, based on the molecules centered at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ respectively, and utilizing the short translation period $a=3·783$ Å. As indicated in Table 5, the shortest intermolecular C···C contacts within these stacks are 3·439 and 3·462 Å for A and 3·506 and 3·510 Å for B. Because the molecules are tilted (*vide infra*) with respect to the direction of translation, the separation between the unsaturated rings is reduced to 3·446 Å (A) and 3·493 Å (B) while the intermolecular distances between Cl atoms related by the translation remain above the sum of their van der Waals radii, 3·6 Å. A very similar crystalline arrangement is encountered in the crystal structure of 2,7-dichlorodibenzo-*p*-dioxin (Boer & North, 1972), where the lattice period is 3·878 Å. Between molecules *A* and *B*, there are two Cl···O separations [Cl(2*A*)···O(*B*), 3·087 Å and Cl(2*B*)···O(*A*), 3·131 Å] which are below the sum of the van der Waals radii (3·2 Å). Although anomalously short (3·4 to 3·5 Å) Cl···Cl contacts were found in crystals of both the 2,7-dichloro (Boer & North, 1972) and 1,2,3,7,8,9-hexachloro (Cantrell, Webb & Mabis, 1969) derivatives, no unusually short intermolecular Cl···Cl distances occur in the 2,3,7,8-tetrachloro compound. The shortest contact of this type is 3·575 Å (Table 5).

Table 5. *Nonhydrogen intermolecular contacts less than* 3·6 Å

	Atom 1	Atom 2	Distance	Transform, atom 2
AB	Cl(2*A*)	O(*B*)	3·087 Å	$1-x, \; -y, \; 1-z$
	Cl(2*B*)	O(*A*)	3·131	$-x, \; 1-y, \; 1-z$
	Cl(3*A*)	Cl(2*B*)	3·575	$-x, \; -y, \; 1-z$
	Cl(2*B*)	C(1*A*)	3·551	$-x, \; 1-y, \; 1-z$
	Cl(2*B*)	C(6*A*)	3·559	$-x, \; 1-y, \; 1-z$
AA	C(2*A*)	C(3*A*)	3·462	$x+1, \; y, \; z$
	C(6*A*)	C(5*A*)	3·439	$x+1, \; y, \; z$
BB	C(4*B*)	C(3*B*)	3·510	$x+1, \; y, \; z$
	C(6*B*)	C(1*B*)	3·506	$x+1, \; y, \; z$
	C(2*B*)	Cl(2*B*)	3·545	$x+1, \; y, \; z$
	C(5*B*)	O(*B*)	3·497	$-x, \; 1-y, \; 1-z$

The molecules are very nearly planar and approximate *mmm* (D_{2h}) symmetry. The least-squares planes through the nonhydrogen atoms of the two molecules are described in Table 6 (Gvildys, 1965*b*). Some of the deviations from this plane, (which range up to 0·034 Å) appear to be statistically significant and are attributed to crystal packing effects. Molecular planes *A* and *B* form respective angles of 24·6 and 22·6° with the *x* axis.

Table 6. *Deviations from least-squares molecular planes for* 2,3,7,8-*tetrachlorodibenzo-p-dioxin*

The planes, defined by the equations $3{\cdot}446x-2{\cdot}851y-6{\cdot}188z=0$ for molecule *A* and $3{\cdot}493x+1{\cdot}467y+3{\cdot}626z=4{\cdot}293$ for molecule *B*, were calculated with the hydrogen atoms excluded. Deviations for the atoms related by the center of symmetry are equal in magnitude but opposite in sign.

Atom	Molecule *A*	Molecule *B*
Cl(2)	0·017 Å	0·018 Å
Cl(3)	−0·016	0·005
O	0·034	−0·005
C(1)	0·004	−0·015
C(2)	−0·007	−0·005
C(3)	0·005	−0·005
C(4)	0·001	−0·008
C(5)	−0·004	−0·008
C(6)	0·007	−0·014
H(1)	0·074	−0·010
H(4)	−0·019	0·001

Chemically equivalent bond distances and angles show very satisfactory agreement. For example the four C–Cl bond distances are 1·726, 1·727, 1·728 and 1·730 Å, while the four unique C–O bonds have values 1·377, 1·378, 1·378 and 1·379 Å. Consistency within the four chemically distinct types of C–C bonds is nearly as good; for type C(1)–C(2), values are 1·381, 1·382, 1·383, and 1·384 Å; for C(2)–C(3), 1·383 and 1·388 Å, for C(4)–C(5), 1·374, 1·376, 1·376, and 1·379 Å, and finally for C(5)–C(6) 1·386 and 1·388 Å. The C–H bonds, which have larger standard errors (±0·02 Å), range from 0·97 to 1·03 Å and are subject to the usual systematic shortening from the true internuclear separation due to the bias of electron density from the hydrogen nucleus into the bonding region. The C–O–C angles in the central ring are 115·6 and

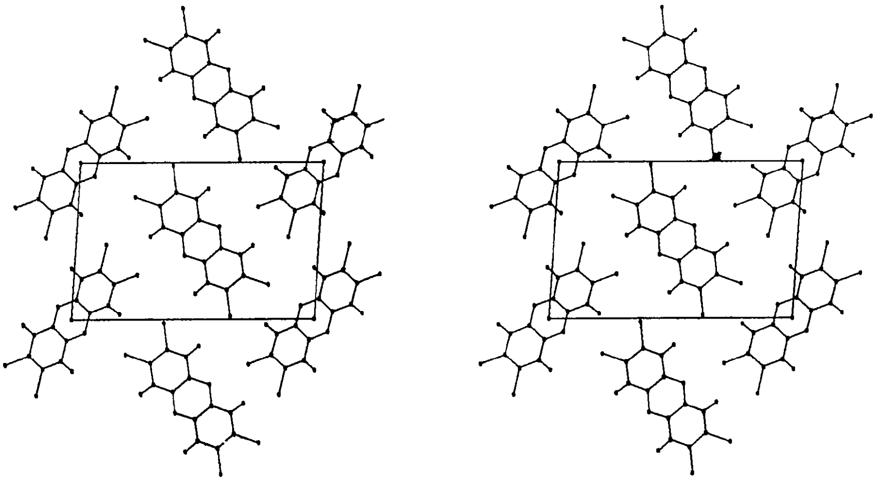

Fig. 2. Stereoscopic view of molecular packing in the *yz* plane of 2,3,7,8,-tetrachlorodibenzo-*p*-dioxin. The parallelogram represents the outline of the triclinic cell.

115·8°; as a result the C–C–O angles in the heterocycle are slightly larger than the trigonal angle and average 122·2°. The internal angles in the benzene rings are all very close to 120°. Repulsion between adjacent chlorine substituents may account for some opening of the C(2)–C(3)–Cl(3) and C(3)–C(2)–Cl(2) angles, which average 121·0°.

The chlorine atoms show large thermal amplitudes within the molecular plane and approximately perpendicular to the C–Cl bonds (Fig. 1). The oxygen atoms also display marked anisotropy, with the largest components directed approximately along the *a* axis or roughly normal to the molecular plane. The carbon atoms for the most part exhibit moderate anisotropy. Rigid-body analysis of the X-ray thermal parameters in 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and some other chlorinated dioxins will be discussed elsewhere.

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The Molecular and Crystal Structure of $KHCO_3.MgCO_3.4H_2O$

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$KHCO_3.MgCO_3.4H_2O$ is triclinic; $a=6{\cdot}713$, $b=7{\cdot}337$, $c=5{\cdot}364$ Å; $\alpha=108{\cdot}2$, $\beta=108{\cdot}9$, $\gamma=59{\cdot}6°$. Measured density $=1{\cdot}99$ g.cm^{-3}, $M=256$, $Z=1$. Space group possibly $P\bar{1}$. With K at 0,0,0, Mg is at $0,\frac{1}{2},\frac{1}{2}$. The Mg atom is in octahedral, the K atom in 12-fold oxygen surrounding. The two carbonate groups are centrosymmetrically arranged with the very short O···O distance of 2·42 Å. If the space group is indeed $P\bar{1}$ then the one acid hydrogen atom should be at the centre, $\frac{1}{2}$,0,0, forming a symmetrical hydrogen bond.

During a vain attempt to synthesize the apparently extinct mineral lansfordite, $MgCO_3.5H_2O$, after the method of Menzel & Brückner (1930), colourless triclinic crystals were formed. Quantitative X-ray spectrometry showed a K content of $15{\cdot}1 \pm 0{\cdot}3$ %, and a Mg content of $9{\cdot}2 \pm 0{\cdot}4$ %. The carbonate content of a probably impure sample was determined by titration to be 37%. Cell constants were found from Weissenberg zero-layer diagrams about three axes, with Cu $K\alpha$ radiation and calibrated with powder lines of Al.

$$a=6{\cdot}713\ (3)\ \text{Å} \qquad \alpha=108{\cdot}18\ (3)°$$
$$b=7{\cdot}337\ (3) \qquad \beta=108{\cdot}92\ (3)$$
$$c=5{\cdot}364\ (1) \qquad \gamma=59{\cdot}57\ (2)$$

The density, determined by suspension, was 1·99 (1) g.cm^{-3}. This gives a cell formula weight of 256·4,