

The Crystal Structure of a Symmetrical 12-Oxa[4.4.3]propella-2,4,7,9-tetraene Bis-irontricarbonyl, $C_{18}H_{12}O_7Fe_2$ *

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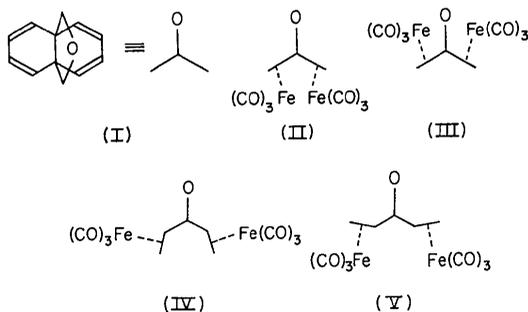
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(Received 31 December 1970)

This symmetrical 12-oxa[4.4.3]propella-2,4,7,9-tetraene bis-irontricarbonyl complex, $C_{18}H_{12}O_7Fe_2$, m.p. 200–204°C, crystallizes in the monoclinic space group $C2/c$ with eight half-molecules in a unit cell of dimensions $a=20.791$ (3), $b=7.173$ (1), $c=12.625$ (2) Å; $\beta=111.42$ (2)°. The densities are: $D_x=1.713$ g.cm⁻³, $D_m=1.709$ g.cm⁻³. The structure was determined by the heavy-atom method from data collected at room temperature on a four-circle diffractometer using the $\theta/2\theta$ scan technique. It was refined by the least-squares method to $R=4.5\%$ for 1323 observed reflexions. Each iron atom is complexed to a butadiene group of four planar carbon atoms of the ligand with the following C–C bond lengths, 1.413 (6), 1.401 (6), 1.422 (6) Å.

Introduction

Treatment of the tetraenic ether (I) with diironnonacarbonyl afforded five organometallic complexes (Altman, Cohen, Maymon, Petersen, Reshef & Ginsburg, 1969), one of them with m.p. 200–204°C. Its nuclear magnetic resonance spectrum suggested that it was a symmetrical bis-irontricarbonyl derivative of structure (II) or (III). This X-ray analysis was carried out in order to resolve this ambiguity. Its results, which showed the structure to be (III) or more clearly shown in (IV) and Fig. 2, were reported in a preliminary communication (Birnbaum, Altman, Maymon & Ginsburg, 1970). In this structure as well as in others in which an irontricarbonyl group is complexed to a cyclic substituted butadiene (*e.g.* see Churchill & Mason, 1967*a*) the ring moiety attached to the outer atoms of the diene system is always bent away from the irontricarbonyl group. The conformation of the six-membered rings of (II) is therefore likely to be as shown in (V).



Crystal data

Symmetrical 12-oxa[4.4.3]propella-2,4,7,9-tetraene bis-irontricarbonyl, $C_{18}H_{12}O_7Fe_2$, F.W. 451.99, m.p. 200–204°C

Monoclinic:

$a=20.791$ (3), $b=7.173$ (1), $c=12.625$ (2) Å;
 $\beta=111.42$ (2)°.

$V=1752.8$ Å³ [Cu $K\alpha_1$ ($\lambda=1.54051$ Å) and Cu $K\alpha_2$ ($\lambda=1.54433$ Å) radiations were used]. $D_m=1.709$ g.cm⁻³ (by flotation in aqueous potassium iodide), $D_x=1.713$ g.cm⁻³, $Z=4$. $F(000)=912$.

Systematic absences:

hkl absent when $h+k$ is odd and $h0l$ absent when l is odd. Possible space groups Cc and $C2/c$. $C2/c$ determined by refinement. Linear absorption coefficient $\mu(\text{Mo } K\alpha)=17.3$ cm⁻¹.

Experimental

The crystals were yellow, long prismatic and one, cut to size 0.19 × 0.24 × 0.31 mm, was mounted along the b (elongated) axis. The cell dimensions and the intensities were measured with an automated four-circle diffractometer (Picker) equipped with a scintillation counter and a pulse-height analyser. Ni-filtered Cu $K\alpha$ radiation was used to measure the cell dimensions. Their values are weighted averages obtained from measurements of axial reflexions and the e.s.d.'s were derived from r.m.s. deviations. The intensity data were obtained by using Nb-filtered Mo $K\alpha$ radiation and the moving-crystal moving-counter ($\theta/2\theta$) scan technique. A 2.0° scan was used for reflexions with $2\theta \leq 35^\circ$ and a 2.4° scan for those with $35^\circ < 2\theta \leq 55^\circ$. The scans were symmetrical and the background was measured for 20 sec on each side of the scan. When the count rate exceeded 20,000 c.p.s. the current was lowered and, when neces-

* Issued as N.R.C.C. No. 12293.

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sary, brass attenuation filters were used. A standard reflexion, 008, was measured at intervals of approximately 30 reflexions and used to scale the data. There was no appreciable change in its intensity during the collection of data. Of the 2008 independent reflexions with $2\theta \leq 55^\circ$, 1325 (66%) were observed above threshold value. The threshold was taken as a net count of 150 or 10% of the background, whichever was higher. The intensities were corrected for Lorentz and polarization factors but no absorption correction was applied, the minimum and maximum transmission coefficients (μt) being 0.33 and 0.54 respectively.

Structure determination

The structure was solved by the heavy-atom method. The statistics of the normalized structure factors (Table 1) show values which are intermediate between those expected for non-centrosymmetric and centrosymmetric space groups. Therefore, one could not distinguish between the space groups Cc and $C2/c$. However, the latter was assumed and at the end of the refinement this assumption proved to be correct.

Table 1. *Statistics of the E's*

		Theoretical values		
	This structure	Centrosymmetric	Non-centrosymmetric	
$\langle E \rangle$	0.825	0.798	0.886	
$\langle E ^2 \rangle$	0.998	1.000	1.000	
$\langle E^2 - 1 \rangle$	0.920	0.968	0.736	
Reflexions with				
$ E < 3$	0.00 %	0.3 %	0.01 %	
$ E < 2$	3.8	5.0	1.8	
$ E < 1$	34.5	32.0	37.0	

In $C2/c$ a diad axis passes through the molecule and thus the asymmetric unit contains half a molecule. The position of the iron atom (0.1395, 0.2065, 0.2500) was determined from a sharpened Patterson map. A Fourier synthesis based on the phases of the iron atom was calculated and all the non-hydrogen atoms were located from it. There were no spurious peaks as high as the ones selected for the molecule. Inclusion of the carbon and oxygen atoms in the calculation of structure factors lowered R from 36 to 19.6%. The scale factor and isotropic thermal parameter ($B = 3.41 \text{ \AA}^2$) used in these calculations were derived from a Wilson plot.

Structure refinement

Coordinates, thermal parameters, and the scale factor were refined by the block-diagonal approximation of the least-squares method, minimizing the expression $\sum w(|F_o| - |F_c|)^2$. The matrices used were 9×9 for coordinates and thermal parameters (4×4 for isotropic thermal motion) of each atom. The scale factor and the overall isotropic thermal parameter were refined by a

2×2 matrix. A shift factor of 0.8 was used throughout the refinement.

Anomalous scattering corrections ($\Delta f' = 0.37$, $\Delta f'' = 0.92$) were applied to the scattering curve of iron. The hydrogen atoms were located on peaks varying in height from 0.42 to 0.70 $e.\text{\AA}^{-3}$ in a difference Fourier synthesis, and subsequently refined with isotropic thermal parameters. All other atoms were refined with anisotropic thermal parameters. The following weighting scheme, chosen so as to reflect the trends in $|\Delta F|$'s, was introduced at this stage:

$$\begin{aligned} \sqrt{w} &= \sqrt{w_1} \cdot \sqrt{w_2} \\ \text{where } \sqrt{w_1} &= (|F_o|/p_1)^{p_2} & \text{when } |F_o| \leq p_1 \\ &= (p_1/|F_o|)^{1/2} & \text{when } |F_o| > p_1 \\ \text{and } \sqrt{w_2} &= (\sin^2 \theta/p_3)^{1/2} & \text{when } \sin^2 \theta \leq p_3 \\ &= 1 & \text{when } \sin^2 \theta > p_3. \end{aligned}$$

The parameters were adjusted during the refinement in order to make $w(\Delta F)^2$ as linear as possible with respect to $|F_o|$ and $\sin^2 \theta$. The final values were $p_1 = 28.0$, $p_2 = 1.10$ and $p_3 = 0.050$.

The refinement converged to an R value of 4.54% ($R' = (\sum w(\Delta F)^2 / \sum w F_o^2)^{1/2} = 4.96\%$) for 1323 observed reflexions; two reflexions were excluded due to poor agreement between observed and calculated structure factors. After the last cycle of refinement all parameter shifts were less than 0.1σ .

The final difference Fourier map showed no significant features except in the vicinity of the Fe atom (Fig. 1). In addition to the peaks and valleys shown in

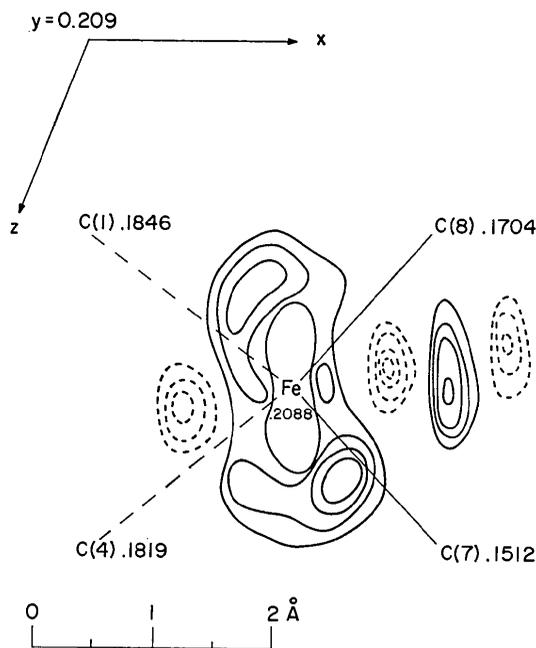


Fig. 1. Section of the final difference Fourier map parallel to (010). The y coordinates of the atoms are marked. Contours are drawn at intervals of $0.1 e.\text{\AA}^{-3}$ and start at $\pm 0.3 e.\text{\AA}^{-3}$. The e.s.d. of this map is $0.11 e.\text{\AA}^{-3}$ (Cruickshank, 1949).

Table 2. Final fractional coordinates and thermal parameters (\AA^2)

(a) Non-hydrogen atoms

The thermal-vibration parameters are expressed as

$$\exp [-2\pi^2(U^{11}h^2a^*2 + U^{22}k^2b^*2 + U^{33}l^2c^*2 + 2U^{23}klb^*c^* + 2U^{13}hla^*c^* + 2U^{12}hka^*b^*)]$$

Positional parameters are multiplied by 10^4 and thermal parameters by 10^3 .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ¹¹	<i>U</i> ²²	<i>U</i> ³³	2 <i>U</i> ²³	2 <i>U</i> ¹³	2 <i>U</i> ¹²
Fe	1383.4 (3)	2088.1 (9)	2468.2 (5)	34.2 (2)	41.9 (3)	43.7 (3)	-18.4 (7)	24.2 (5)	3.7 (6)
C(1)	340 (2)	1846 (6)	1389 (3)	37 (2)	45 (3)	33 (2)	-9 (4)	18 (3)	-3 (4)
C(2)	623 (2)	118 (6)	1877 (4)	41 (2)	34 (2)	48 (3)	-23 (4)	20 (4)	1 (4)
C(3)	894 (2)	90 (6)	3068 (4)	36 (2)	42 (3)	47 (3)	8 (4)	16 (4)	8 (4)
C(4)	840 (2)	1819 (6)	3581 (3)	32 (2)	45 (3)	34 (2)	-8 (4)	10 (3)	-3 (4)
C(5)	152 (2)	2853 (6)	3158 (3)	38 (2)	31 (2)	34 (2)	-7 (4)	20 (3)	-3 (4)
C(6)	223 (2)	4917 (7)	3479 (5)	43 (2)	42 (3)	67 (3)	-29 (4)	52 (4)	-13 (4)
C(7)	2205 (2)	1512 (8)	3535 (4)	37 (2)	73 (3)	51 (3)	-40 (5)	27 (4)	2 (4)
C(8)	1692 (3)	1704 (8)	1340 (4)	46 (3)	72 (4)	54 (3)	-31 (5)	25 (4)	-5 (5)
C(9)	1476 (2)	4572 (7)	2541 (5)	42 (3)	50 (3)	84 (4)	-19 (6)	65 (5)	-15 (4)
O(1)	0 (0)	5964 (7)	2500 (0)	157 (7)	29 (3)	92 (5)	0 (0)	74 (9)	0 (0)
O(2)	2721 (2)	1119 (8)	4210 (4)	45 (2)	122 (4)	70 (3)	-34 (5)	7 (3)	34 (4)
O(3)	1877 (2)	1466 (9)	609 (4)	76 (3)	158 (5)	65 (3)	-69 (6)	74 (4)	-19 (6)
O(4)	1560 (2)	6127 (6)	2590 (5)	77 (3)	49 (2)	178 (5)	-35 (6)	149 (6)	-31 (4)

this figure there were peaks above and below the iron atom at distances of 0.8–1.0 Å from it. These features may possibly be due to the non-sphericity of the iron orbitals as well as to series termination errors.

In order to verify the space group, the structure was also refined in *Cc*. Since the parameters were oscillating a shift factor of 0.5 was used. The ratio of observed reflexions to refined parameters is lower in this space group and therefore the hydrogen atoms were not refined but included in fixed positions. The ratio of the two *R'* values is 0.999 and according to Hamilton's (1965) test the originally chosen space group *C2/c* is definitely correct.

The scattering factors of Hanson, Herman, Lea & Skillman (1964) were used throughout the analysis for carbon and oxygen atoms. The values for neutral iron were obtained from Cromer & Waber (1965) and Cromer (1965), and those for bonded hydrogen atoms were taken from Stewart, Davidson & Simpson (1965).

The final coordinates and thermal parameters are listed in Table 2. The listed e.s.d. values were obtained from the inverse of the least-squares matrix. Table 3 shows the observed and calculated structure factors. The unobserved reflexions are marked with an asterisk. They were given the threshold value but were excluded from the least-squares refinement. Inspection of the *F_o* and *F_c* values of strong reflexions did not reveal any extinction effect and no correction was applied.

Table 2 (cont.)

(b) Hydrogen atoms

All values are multiplied by 10^3

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(11)	22 (3)	201 (7)	56 (4)	46 (12)
H(21)	70 (2)	-92 (6)	151 (4)	37 (11)
H(31)	116 (3)	-97 (7)	350 (4)	48 (13)
H(41)	109 (3)	196 (8)	441 (5)	59 (15)
H(61)	-6 (4)	531 (10)	392 (6)	84 (20)
H(62)	68 (3)	520 (8)	388 (4)	53 (14)

Thermal-vibration analysis

The thermal vibration of the entire complex as well as of the ligand and the irontricarbonyl group, separately, were analysed in terms of the rigid-body tensors of translation (*T*), libration (*L*) and screw motion (*S*) (Schomaker & Trueblood, 1968). However, only the vibration of the irontricarbonyl group fits this model, the value of $\sigma U_{\text{calc}} = [\sum (\Delta U^{ij})^2 / (n-s)]^{1/2}$ being 0.0059\AA^2 (compared to 0.0118 and 0.0110\AA^2 for the entire molecule and the ligand respectively) and $\langle \sigma U_{\text{obs}}^{ij} \rangle$ being 0.0034\AA^2 . The positional parameters of the irontricarbonyl group were corrected for the libration motion and the resulting bond lengths are shown in parentheses in Fig. 3. There was no appreciable change in the bond angles and these are therefore not shown.

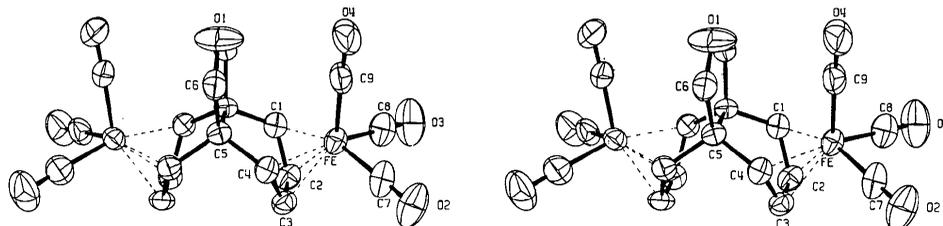


Fig. 2. Stereoscopic view of the complex. The thermal ellipsoids enclose 50% probability.

Table 3. Observed and calculated structure factors

All F values are multiplied by 10. Unobserved reflexions are marked with an asterisk. The 21,3,4 and 21,3,6 reflexions are excluded from the least-squares calculations due to poor agreement between observed and calculated values.

k	l	h	F _o	F _c	k	l	h	F _o	F _c	k	l	h	F _o	F _c	k	l	h	F _o	F _c
0	0	0	1.449	1.455	0	0	1	0.999	1.000	0	0	1	0.999	1.000	0	0	1	0.999	1.000
0	0	2	0.127	0.104	0	0	2	0.120	0.111	0	0	2	0.120	0.111	0	0	2	0.120	0.111
0	0	4	0.345	0.264	0	0	4	0.309	0.287	0	0	4	0.309	0.287	0	0	4	0.309	0.287
0	0	6	0.589	0.461	0	0	6	0.528	0.483	0	0	6	0.528	0.483	0	0	6	0.528	0.483
0	0	8	0.847	0.647	0	0	8	0.762	0.703	0	0	8	0.762	0.703	0	0	8	0.762	0.703
0	0	10	1.112	0.847	0	0	10	1.003	0.924	0	0	10	1.003	0.924	0	0	10	1.003	0.924
0	0	12	1.384	1.098	0	0	12	1.252	1.142	0	0	12	1.252	1.142	0	0	12	1.252	1.142
0	0	14	1.661	1.363	0	0	14	1.507	1.363	0	0	14	1.507	1.363	0	0	14	1.507	1.363
0	0	16	1.942	1.641	0	0	16	1.752	1.572	0	0	16	1.752	1.572	0	0	16	1.752	1.572
0	0	18	2.227	1.931	0	0	18	2.000	1.817	0	0	18	2.000	1.817	0	0	18	2.000	1.817
0	0	20	2.516	2.232	0	0	20	2.250	2.072	0	0	20	2.250	2.072	0	0	20	2.250	2.072
0	0	22	2.808	2.544	0	0	22	2.495	2.283	0	0	22	2.495	2.283	0	0	22	2.495	2.283
0	0	24	3.103	2.866	0	0	24	2.782	2.524	0	0	24	2.782	2.524	0	0	24	2.782	2.524
0	0	26	3.401	3.200	0	0	26	3.070	2.775	0	0	26	3.070	2.775	0	0	26	3.070	2.775
0	0	28	3.701	3.545	0	0	28	3.358	3.036	0	0	28	3.358	3.036	0	0	28	3.358	3.036
0	0	30	4.003	3.901	0	0	30	3.646	3.302	0	0	30	3.646	3.302	0	0	30	3.646	3.302
0	0	32	4.307	4.268	0	0	32	3.934	3.573	0	0	32	3.934	3.573	0	0	32	3.934	3.573
0	0	34	4.613	4.646	0	0	34	4.222	3.848	0	0	34	4.222	3.848	0	0	34	4.222	3.848
0	0	36	4.921	5.035	0	0	36	4.510	4.129	0	0	36	4.510	4.129	0	0	36	4.510	4.129
0	0	38	5.231	5.435	0	0	38	4.798	4.415	0	0	38	4.798	4.415	0	0	38	4.798	4.415
0	0	40	5.543	5.845	0	0	40	5.086	4.702	0	0	40	5.086	4.702	0	0	40	5.086	4.702
0	0	42	5.857	6.265	0	0	42	5.374	4.989	0	0	42	5.374	4.989	0	0	42	5.374	4.989
0	0	44	6.173	6.695	0	0	44	5.662	5.276	0	0	44	5.662	5.276	0	0	44	5.662	5.276
0	0	46	6.491	7.135	0	0	46	5.950	5.564	0	0	46	5.950	5.564	0	0	46	5.950	5.564
0	0	48	6.811	7.585	0	0	48	6.238	5.852	0	0	48	6.238	5.852	0	0	48	6.238	5.852
0	0	50	7.133	8.045	0	0	50	6.526	6.140	0	0	50	6.526	6.140	0	0	50	6.526	6.140
0	0	52	7.457	8.515	0	0	52	6.814	6.428	0	0	52	6.814	6.428	0	0	52	6.814	6.428
0	0	54	7.783	8.995	0	0	54	7.102	6.716	0	0	54	7.102	6.716	0	0	54	7.102	6.716
0	0	56	8.111	9.485	0	0	56	7.390	7.004	0	0	56	7.390	7.004	0	0	56	7.390	7.004
0	0	58	8.441	9.985	0	0	58	7.678	7.292	0	0	58	7.678	7.292	0	0	58	7.678	7.292
0	0	60	8.773	10.495	0	0	60	7.966	7.580	0	0	60	7.966	7.580	0	0	60	7.966	7.580
0	0	62	9.107	11.015	0	0	62	8.254	7.868	0	0	62	8.254	7.868	0	0	62	8.254	7.868
0	0	64	9.443	11.545	0	0	64	8.542	8.156	0	0	64	8.542	8.156	0	0	64	8.542	8.156
0	0	66	9.781	12.085	0	0	66	8.830	8.444	0	0	66	8.830	8.444	0	0	66	8.830	8.444
0	0	68	10.121	12.635	0	0	68	9.118	8.732	0	0	68	9.118	8.732	0	0	68	9.118	8.732
0	0	70	10.463	13.195	0	0	70	9.406	9.020	0	0	70	9.406	9.020	0	0	70	9.406	9.020
0	0	72	10.807	13.765	0	0	72	9.694	9.308	0	0	72	9.694	9.308	0	0	72	9.694	9.308
0	0	74	11.153	14.345	0	0	74	9.982	9.596	0	0	74	9.982	9.596	0	0	74	9.982	9.596
0	0	76	11.501	14.935	0	0	76	10.270	9.884	0	0	76	10.270	9.884	0	0	76	10.270	9.884
0	0	78	11.851	15.535	0	0	78	10.558	10.172	0	0	78	10.558	10.172	0	0	78	10.558	10.172
0	0	80	12.203	16.145	0	0	80	10.846	10.460	0	0	80	10.846	10.460	0	0	80	10.846	10.460
0	0	82	12.557	16.765	0	0	82	11.134	10.748	0	0	82	11.134	10.748	0	0	82	11.134	10.748
0	0	84	12.913	17.395	0	0	84	11.422	11.036	0	0	84	11.422	11.036	0	0	84	11.422	11.036
0	0	86	13.271	18.035	0	0	86	11.710	11.324	0	0	86	11.710	11.324	0	0	86	11.710	11.324
0	0	88	13.631	18.685	0	0	88	12.000	11.612	0	0	88	12.000	11.612	0	0	88	12.000	11.612
0	0	90	13.993	19.345	0	0	90	12.290	11.900	0	0	90	12.290	11.900	0	0	90	12.290	11.900
0	0	92	14.357	20.015	0	0	92	12.580	12.188	0	0	92	12.580	12.188	0	0	92	12.580	12.188
0	0	94	14.723	20.695	0	0	94	12.870	12.476	0	0	94	12.870	12.476	0	0	94	12.870	12.476
0	0	96	15.091	21.385	0	0	96	13.160	12.764	0	0	96	13.160	12.764	0	0	96	13.160	12.764
0	0	98	15.461	22.085	0	0	98	13.450	13.052	0	0	98	13.450	13.052	0	0	98	13.450	13.052
0	0	100	15.833	22.795	0	0	100	13.740	13.340	0	0	100	13.740	13.340	0	0	100	13.740	13.340
0	0	102	16.207	23.515	0	0	102	14.030	13.628	0	0	102	14.030	13.628	0	0	102	14.030	13.628
0	0	104	16.583	24.245	0	0	104	14.320	13.916	0	0	104	14.320	13.916	0	0	104	14.320	13.916
0	0	106	16.961	24.985	0	0	106	14.610	14.204	0	0	106	14.610	14.204	0	0	106	14.610	14.204
0	0	108	17.341	25.735	0	0	108	14.900	14.492	0	0	108	14.900	14.492	0	0	108	14.900	14.492
0	0	110	17.723	26.495	0	0	110	15.190	14.780	0	0	110	15.190	14.780	0	0	110	15.190	14.780
0	0	112	18.107	27.265	0	0	112	15.480	15.068	0	0	112	15.480	15.068	0	0	112	15.480	15.068
0	0	114	18.493	28.045	0	0	114	15.770	15.356	0	0	114	15.770	15.356	0	0	114	15.770	15.356
0	0	116	18.881	28.835	0	0	116	16.060	15.644	0	0	116	16.060	15.644	0	0	116	16.060	15.644
0	0	118	19.271	29.635	0	0	118	16.350	15.932	0	0	118	16.350	15.932	0	0	118	16.350	15.932
0	0	120	19.663	30.445	0	0	120	16.640	16.220	0	0	120	16.640	16.220	0	0	120	16.640	16.220
0	0	122	20.057	31.265	0	0	122	16.930	16.508	0	0	122	16.930	16.508	0	0	122	16.930	16.508
0	0	124	20.453	32.095	0	0	124	17.220	16.796	0	0	124	17.220	16.796	0	0	124	17.220	16.796
0	0	126	20.851	32.935	0	0	126	17.510	17.084	0	0	126	17.510	17.084	0	0	126	17.510	17.084
0	0	128	21.251	33.785	0	0	128	17.800	17.372	0	0	128	17.800	17.372	0	0	128	17.800	17.372
0	0	130	21.653	34.645	0	0	130	18.090	17.660	0	0	130	18.090	17.660	0	0	130	18.090	17.660
0	0	132	22.057	35.515	0	0	132	18.380	17.948	0	0	132	18.380	17.948	0	0	132	18.380	17.948
0	0	134	22.463	36.395	0	0	134	18.670	18.236	0	0	134	18.670	18.236	0	0	134	18.670	18.236
0	0	136	22.871	37.285	0	0	136	18.960	18.524	0	0	136	18.960	18.524	0	0	136	18.960	18.524
0	0	138	23.281	38.185	0	0	138	19.250	18.812	0	0	138	19.250	18.812	0	0	138	19.250	18.812
0	0	140	23.693	39.095	0	0	140	19.540	19.100	0	0	140	19.540	19.100	0	0	140	19.540	19.100
0	0	142	24.107	40.015	0	0	142	19.830	19.388	0	0	142	19.830	19.388	0	0	142	19.830	19.388

Table 6. *Weighted least-squares planes*

Plane 1	Δ	Plane 2	Δ	Plane 3	Δ	Plane 4	Δ	Plane 5	Δ
O(1)	0.000 Å	C(1)	0.000 Å	C(1)	0.003 Å	C(1)	-0.023 Å	C(7)	0.0 Å
C(5)	0.002	C(2)	0.000	C(4)	-0.003	C(4)	0.022	C(8)	0.0
C(5')	-0.002	C(3)	-0.003	C(5)	0.005	C(7)	-0.034	C(9)	0.0
C(6)	-0.002	C(4)	0.001	C(5')	-0.005	C(8)	0.038	Fe*	-0.920
C(6')	0.002	H(21)	0.106			O(2)*	-0.253	O(2)*	0.568
		H(31)	0.113			O(3)*	-0.112	O(3)*	0.571
		H(11)*	0.157			Fe*	0.278	O(4)*	0.622
		H(41)*	0.150			C(9)*	2.067		
		C(5)*	-0.977			O(4)*	3.191		
		C(5')*	-0.986			M(2,3)*	-1.217		
		Fe*	1.643						
r.m.s.d.=0.002		r.m.s.d.=0.063		r.m.s.d.=0.004		r.m.s.d.=0.030		r.m.s.d.=0.0	
$\chi^2=0.6$		$\chi^2=8.9$		$\chi^2=3.3$		$\chi^2=130.1$		$\chi^2=0.0$	

* Atoms excluded from the calculation of the plane.

Table 6 (cont.)

Equations of the planes are of the type
 $hx + ky + lz = m$ where x, y, z
 are fractional monoclinic coordinates

Plane	$h(\text{Å})$	$k(\text{Å})$	$l(\text{Å})$	$m(\text{Å})$
1:	20.791	0.000	-4.764	-1.190
2:	19.980	1.994	-4.525	0.419
3:	10.603	6.169	-2.375	1.167
4:	1.206	7.159	0.015	1.387
5:	18.712	3.127	-4.091	3.151

Some dihedral angles between the planes

$\angle_{1,2}$	$\angle_{1,3}$	$\angle_{2,3}$	$\angle_{1,4}$	$\angle_{2,4}$	$\angle_{2,5}$
16.1	59.3	43.2	93.3	109.4	9.7°

local C_{2v} symmetry. The six-membered cyclohexadiene rings are boat-shaped and thus different from what would have been expected in uncomplexed form. The torsional angles (Fig. 4) demonstrate that the rings are flattened as compared to an ideal cyclohexane boat in which two of the calculated torsional angles are 0° and four are $\pm 54^\circ$ (Bucourt & Hainaut, 1965). Each iron atom is bonded to a planar 'butadiene'

moiety [C(1), C(2), C(3), C(4)] and the atoms C(1) and C(4) have a certain amount of sp^3 character (plane 2 in Table 6). The displacements of H(11) and H(41) from this plane, towards the iron atom, correspond to a bend of 9° . In agreement with this the average of the two bond lengths C(1)-C(5') and C(4)-C(5) [1.525 (4) Å] lies between the values for $C_{sp^3}-C_{sp^3}$ and for $C_{sp^3}-C_{sp^2}$ bonds (1.537 ± 0.005 and 1.505 ± 0.005 Å, respectively; Sutton, 1965). The three 'butadiene' bonds are equal within experimental error at a 0.1% significance level and their average length is 1.412 (3) Å, a result which argues in favour of delocalization of electrons. However, there is a slight indication that C(2)-C(3) [1.401 (6) Å] is shorter than the two bonds C(1)-C(2) and C(3)-C(4) [average length 1.418 (4) Å], the $\Delta/\sigma(\Delta)$ being 2.4. This indication prevails in most other structures and thus appears to be real.

As usual, the distances from the iron atom to the 'inner' atoms [C(2) and C(3)] are equal and their average, 2.051 (4) Å, is significantly shorter than the average, 2.107 (3) Å, of the two equal Fe...C distances to the 'outer' atoms [C(1) and C(4)]. Similarly, the distances from Fe to the midpoints of the three bonds

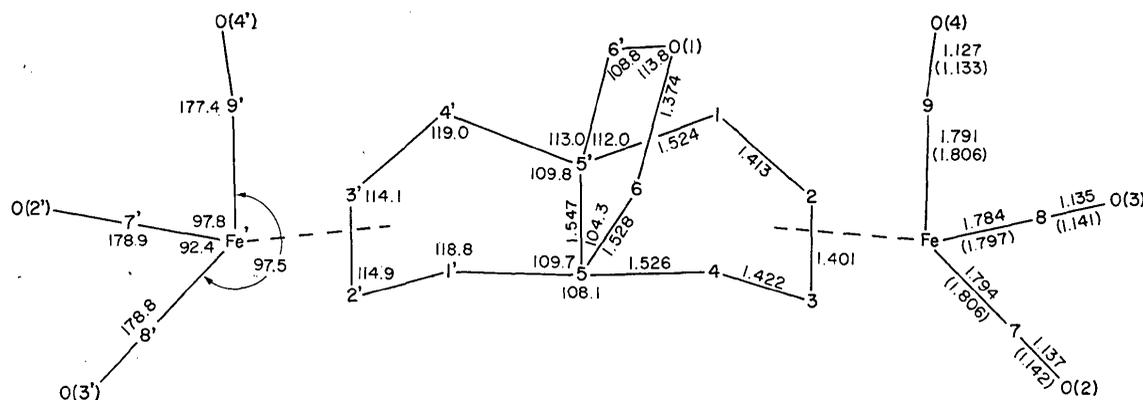


Fig. 3. Bond lengths and angles. The values given in parentheses are corrected for thermal vibration. The e.s.d.'s of bond lengths are 0.006 Å for C-C and C-O; 0.005 Å for Fe-C; 0.007 Å for C=O and those of bond angles are 0.3-0.4° in the ligand, 0.2-0.3° at Fe, 0.5° at C in the irontricarbonyl group.

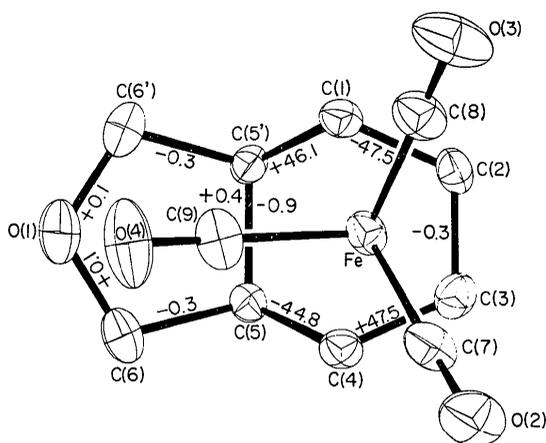


Fig. 4. A parallel projection, viewed along the normal to the 'butadiene' plane. The thermal ellipsoids enclose 30% probability (Johnson, 1965). The torsional angles (Klyne & Prelog, 1960) in the rings are marked; their e.s.d.'s (Huber, 1961) are in the range 0.4–0.6°.

fall into two classes, $\text{Fe}\cdots\text{M}(2,3)$ [1.928 (5) Å] being shorter than the average [1.955 (3) Å] of the two equal $\text{Fe}\cdots\text{M}(1,2)$ and $\text{Fe}\cdots\text{M}(3,4)$ distances.

On the basis of the refined atomic positions the five-membered ring is planar. However, O(1) has a very large thermal-vibration component ($U=0.1641$ Å²) normal to this ring. Two possible interpretations can be put forward: (i) either O(1) is continuously flipping back and forth or (ii) the five-membered ring really occurs in the envelope conformation with O(1) bent to one side in 50% of the molecules in the crystal and to the opposite side in the other 50%. This analysis cannot distinguish between the two possibilities. Either case would account for the bond C(6)–O(1) being considerably shorter than the mean value of 1.426 ± 0.005 Å given by Sutton (1965).

The iron tricarbonyl group has the usual approximate C_{3v} symmetry. The plane through the three carbon atoms [C(7), C(8), C(9)] of each carbonyl group is not quite parallel to the 'butadiene' plane (Table 6). The three Fe–C bonds, as well as the three C≡O bonds, are equal within experimental error and their averages are 1.803 (3) and 1.139 (4) Å respectively. From 20 bonds in related substances (see references above) the corresponding weighted averages were calculated to be 1.779 (4) and 1.147 (4) Å. The agreement is very good for the C≡O bonds while the Fe–C bonds are longer in this structure. This is presumably due to the fact that

the bond lengths in the other structures were not corrected for thermal vibration. The C–Fe–C angles are of two types. The angles C(7)–Fe–C(9) and C(8)–Fe–C(9) have an average value of 97.6 (2)° and are larger than C(7)–Fe–C(8) [92.4 (2)°]. The groups Fe–C(7)–O(2) and Fe–C(8)–O(3) are linear while the Fe–C(9)–O(4) angle [177.4 (5)°] is slightly smaller than 180°. O(4) is bent away from the oxygen atom in the ligand. However, the O(1)···O(4) distance of 3.206 Å does not indicate any van der Waals interaction. Fig. 4 shows how the iron tricarbonyl group overlaps with the ligand.

The packing of the molecules is shown in Fig. 5. There are no intermolecular distances shorter than van der Waals contacts.

I wish to thank Professor D. Ginsburg for suggesting this problem and for supplying me with crystals. I am also indebted to Dr Maria Przybylska for her constant encouragement and interest during this work. The use of the computer programs of Ahmed, Hall, Pippy & Huber (1966), of ORTEP (Johnson, 1965) and of TLS6 (Schomaker & Trueblood, 1968) is gratefully acknowledged.

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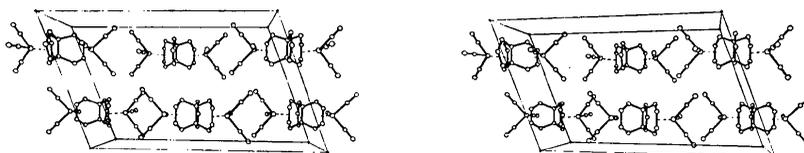


Fig. 5. Stereoscopic diagram. The front, lower left corner is the origin. The directions of the axes are $a \rightarrow$, c^v , c^w .

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The Crystal Structure of the High-Temperature Modification of Potassium Pentaborate

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(Received 10 February 1971)

The high-temperature modification of potassium pentaborate, α - $K_2O \cdot 5B_2O_3$, is orthorhombic with 4 formula units in the unit cell of dimensions $a = 8.383 \pm 0.001$, $b = 8.418 \pm 0.001$, $c = 21.540 \pm 0.003$ Å. The space group is *Pbca*. The calculated density of the phase, 1.93 g.cm^{-3} , is much less than the density of the low-temperature modification, 2.29 g.cm^{-3} , for which the structure was reported previously. The structure in this study was determined and refined by least-squares methods to an *R* value of 0.062 with three-dimensional diffractometer data. The weighted *R* value was 0.038. The structure contains the characteristic double-ring pentaborate groups connected in two separate interpenetrating networks. The bond lengths of the boron–oxygen bond in the planar BO_3 triangle are about 1.320 Å if the adjacent bond to the oxygen atom is from a fourfold coordinated boron atom, and 1.385 Å if the adjacent bond to the oxygen atom is from a threefold coordinated boron atom. The standard deviation for the boron–oxygen bond is 0.006 Å. The potassium ion is surrounded by 8 close oxygen neighbours at distances ranging from 2.770 to 3.139 Å.

Introduction

The crystal structure of the low-temperature modification of potassium pentaborate, β - $K_2O \cdot 5B_2O_3$, was determined previously by Krogh-Moe (1959*a*, 1965). Unit-cell data for the high-temperature modification were also reported (Krogh-Moe, 1959*b*). Because of the great difference in density of these two phases (the ratio of the densities is $\rho_\beta/\rho_\alpha = 1.19$), it was assumed that there might be interesting structural differences between the two phases; therefore, a complete structure determination of the high-temperature modification was undertaken.

Experimental

Crystalline α - $K_2O \cdot 5B_2O_3$ was prepared by fusing potassium carbonate with boric acid in the stoichiometric ratio in a platinum crucible and crystallizing the mixture at 760°C. A single crystal in the shape of a prism bounded by the (100), (010), and (001) faces was used for collecting data. Dimensions of the crystal were $0.0090 \times 0.0095 \times 0.0080$ cm along the *a*, *b*, and *c* axes respectively; the *a* axis was aligned with the goniometer head axis. Data were collected with an on-line

Picker single-crystal automatic diffractometer. Unit-cell dimensions and standard errors $a = 8.383 \pm 0.001$, $b = 8.418 \pm 0.001$, $c = 21.540 \pm 0.003$ Å were obtained by the method of least-squares from angle data recorded at 22°C for 12 high-angle reflections (based on the wavelength 1.5405 Å for $Cu K\alpha_1$). For four formula units of $K_2O \cdot 5B_2O_3$ in the cell, the calculated density is 1.93 g.cm^{-3} . Krogh-Moe (1959*b*) obtained an experimental value of 1.95 g.cm^{-3} for this phase.

Structure determination

The systematic extinction corresponds to that of space group *Pbca*. The experimental intensities were converted in the usual manner to observed structure factors. No correction for absorption was made. With a linear absorption coefficient of 62.9 cm^{-1} , the absorption error in the relative structure factors from a crystal of the above mentioned size and shape will not be large. (A sphere of about the same size would require a maximum relative correction of 2% in the intensities between the high-angle and low-angle limit of the observations.) Preliminary signs for the largest structure factors were determined by the symbolic-