The Crystal Structure of a Symmetrical 12-Oxa[4.4.3]propella-2,4,7,9-tetraene Bis-irontricarbonyl, C₁₈H₁₂O₇Fe₂*

By Karin Bjåmer Birnbaum[†]

Biochemistry Laboratory, National Research Council of Canada, Ottawa, Canada

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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, 1967a) the ring moiety attached to the outer atoms of the diene system is always bent away from the irontricarbonyl group. The conformation of the sixmembered rings of (II) is therefore likely to be as shown in (V).



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Crystal data

Symmetrical 12-oxa[4.4.3]propella-2,4,7,9-tetraene bisirontricarbonyl, C₁₈H₁₂O₇Fe₂, F.W. 451.99, m.p. 200-204°C

Monoclinic: a = 20.791 (3), b = 7.173 (1), c = 12.625 (2) Å; $\beta = 111.42 (2)^{\circ}$.

 $V = 1752.8 \text{ Å}^3$ [Cu $K\alpha_1$ ($\lambda = 1.54051 \text{ Å}$) and Cu $K\alpha_2$ $(\lambda = 1.54433 \text{ Å})$ radiations were used]. $D_m = 1.709$ g.cm⁻³ (by flotation in aqueous potassium iodide), $D_r = 1.713$ 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 μ (Mo K α) = 17.3 cm⁻¹.

Experimental

The crystals were yellow, long prismatic and one, cut to size $0.19 \times 0.24 \times 0.31$ 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 $2\theta \le 35^\circ$ and a 2.4° scan for those with $35^{\circ} < 2\theta \le 55^{\circ}$. 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-

[†] National Research Council Postdoctorate Fellow 1968-1970.

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 $2\theta \le 55^\circ$, 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	0	f the	E's
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			Theore	tical values
		This structure	Centrosym- metric	Non-centro- symmetric
	$\begin{array}{c} \left<  E  \right> \\ \left<  E ^2 \right> \\ \left<  E^2 - 1  \right> \end{array}$	0·825 0·998 0·920	0·798 1·000 0·968	0·886 1·000 0·736
Reflexions with	<i>E</i>   < 3   <i>E</i>   < 2   <i>E</i>   < 1	0·00 % 3·8 34·5	0·3 % 5·0 32·0	0·01 % 1·8 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  $(B=3.41 \text{ Å}^2)$  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  $9 \times 9$  for coordinates and thermal parameters  $(4 \times 4 \text{ for isotropic})$ thermal motion) of each atom. The scale factor and the overall isotropic thermal parameter were refined by a

 $2 \times 2$  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.Å⁻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:

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

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% $(R' = (\sum w(\Delta F)^2 / \sum wF_o^2)^{1/2} = 4.96\%)$  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  $0.1\sigma$ .

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  $0.1 \text{ e.Å}^{-3}$  and start at  $\pm 0.3 \text{ e.Å}^{-3}$ . The e.s.d of this map is  $0.11 \text{ e.Å}^{-3}$  (Cruickshank, 1949).

## Table 2. Final fractional coordinates and thermal parameters (Å²)

(a) Non-hydrogen atoms

The thermal-vibration parameters are expressed as

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

Positional parameters are multiplied by 10⁴ and thermal parameters by 10³.

	x	у	z	$U^{11}$	$U^{22}$	<b>U</b> ³³	$2U^{23}$	$2U^{13}$	$2U^{12}$
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)
<b>C</b> (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)
<b>O</b> (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 103

	x	у	Z	$U_{iso}$
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  $\sigma U_{cale} = [\sum (\Delta U^{ij})^2/(n-s)]^{1/2}$  being 0.0059Å² (compared to 0.0118 and 0.0110Å² for the entire molecule and the ligand respectively) and  $\langle \sigma U_{obs}^{ij} \rangle$ being 0.0034Å². 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.

# CRYSTAL STRUCTURE OF C18H12O7Fe2

# Table 3. Observed and calculated structure factors

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

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6 950 -48 8 1090 72	;	259 -255		2. 115	:	340 -35	1	215 -193	:	291 308	н.	7. 114	H-'	110• 3 9• L•		430 -44	1	1190 -4		292 284	;	260 251
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3 136 180 5 776 -789	1 :	506 -529 930 -32	3	404 421	1	181 194	r.	115 -24	1	114 102	ê	101 -82	1.	108* 84	2 ",	11. L.	, } }	340 -340 220	ç	536 534	1	129 93
7 197 185		2, 1, 2,	н."	112+ -99 3+ L+ -7	°	1184 -13		132 104	<b>"</b> ,	1052 - 999	",	8. L. 7 9217	, 1	9, 1.		334 33	, "·	142 -114		112 -92		15. 110
H= 1, L= -3 1 144 -138	2	329 330 155 -151		1042 1035 528 -551	5	604 627 523 -534	¹	1200 - 30	3	407 -478	:	159 -184	1	98* -3*	2	1140 -7	., ?	274 -230	. ** e	14. 17	3	253 23"
3 270 308 5 633 -637	8	970 18 1140 28	;	332 318 108* 6*	:	980 83 1110 -59	2	1624 1474 953 -892		127 -124	۳,	8. L+ -7	H-5	9, 10 -1		428 -42		200 -274	1	521 507	<b>"</b> `	242 -267
7 990 101 9 1180 -47	"z	73 - 63	^{#•} 1	130 -144	<b>**</b> 2	4. Le 11 148 -130	:	157 -191	;	244 241	:	635 657 302 -305	1	116 -10.	; ;	135 10	8 ** 2	1120 76	°°	117 -120	1	111 104
", 2 ¹³ 272	1	239 252	3	202 205		285 283 41 L+ -11	н.	111* -92 6. L* 1	;	217 -214	н.•	127 104 8, L+ 8	H.'	9, 14 -	, "-ı	251 -24	,*  *	121 -124		2-1 247	<b>.</b> .`	11.1. 112
5 416 416		2	н.	3.18	14	249 -251		384 396	[" <u>1</u>	244 -246	1 5	287 303 970 -71	1 5	113.		300 - 10		080 14		14. 13	;	440 -418
9 1100 -48	Ĭ	88 100	l i	394 404	ו ^	4. 1. 12	1.5	1*5 194	1	542 596		116* -31	1.		· (	11	· · · · ·	12 1. 1		543 434	]	15. 113
1 643 -590		110 125	L.;	246 224	1	225 225	2	47 41	H.			1167 1134	1 ** 1	9. L		71 76	5 . <b>.</b> .	110 -120		14.1		1120 -78
5 214 -216		2. 16	1	530 549	۳.	4+ L+ -17		920	11	410 417		91.0 . 73	1.	10	·	104 39		401		485 -480	44	15. 11.
9 119 40	11	233 -214	1	106* \$1	ž	314 312		1414 -1519		140 -176	`	120111	í ž	-80 -0		671 67	: 1 :	166 147		1164 -47	1.3	221 220
1 137 -107	1 :	98* 50 115* 47	<b>*</b> -,	1. L+ -9 850 -876	°	1144 11	2	565 541 187 16*	1	1744 1673	1	127 -114	ŝ	116* 7		119+ 8		228 232	1 5	1772 1693	1	116* -12*
5 434 439	H= 2	115 139	1	465 468		4, 10 -13	Å	148 153	;	232 215	۳,	300 306	H** 2	279 29	,'   "•'ı	11. 1.		152 -144	:	105* 80		210 - 240
1 254 -256		104* 31	н	3, 1. 10	1	253 244	1°0	484 -889	<b>"</b> 1	392 - 394		342 -349 228 225		209 21		219 -21	; ",	12. 11		171 -105	1	100 100
5 569 602		2, 1 -7		263 -251		194 185	1	129 -132	1 3	523 -512	"°	8. L. 10	н-8	10, 1-	1 '	1090 -11		109 -3	:	402 391 202 -197		1120 -20
9 1200 94	1 5	114 -00	۲.	3. 110		302 293	ì	110+ 32	H•	7. 10	1.4	138 -158	1 -	616 63		191 -17	.   m°	12. 11	<u>الاً ال</u>	419	1 -	102+ -75
1 369 -389		1170 -12		321 - 321	1.4	118+ 29		• • • • • •		A26 846		145 -14		260 25	5	11, 1+		113 105	1:	251 256	<b>*-</b> °	16. 11
5 230 -235		824 44	,	143 -127	2	165 162		188 189	1.1	273 277		209 -221	1.5	1144 111		569 - 44		1094 34	1	314 -370		
H- 1, L		117 -118	1	332 -337	1	1103 -1017	۲.,	0.1····	1	446 479	н,	8. 1. 11		255 26	;   _; ;	332 -31	í, [ 📫	1174 12		1110 -43	۳.	16. 1. 2
3 517 -534	1	2. 18	H-5	115+ -10	1	101+ 100		212 219	;	141 142		212 -230	H. 8	118		341 -51	2	110* -8	1 3	1107 -1157	11	110 04
7 1044 76		264 269	1	509 518		1194 -172		207 217	۳.	1042 -1023	2	95* 40	9	1255 1180		1130 -110		1190 13		339 -134		114 94
1 104 108	8	1040 11	н.,	1094 94 3. L= 12	1	866 8L9 184 174	ŝ	135 -126	1	743 748	".*	155 154		145 122		9CA 89	ti i	216 - 224		219 217	ŝ	310 -30+
5 400 -394 7 259 278	1.	2, L 9 909 - 76	1	1070 -41	;	840 73		85* 50 100* -17	·'	270 -274	2	368 375 341 331	H-	109 -130	\$  \$	196 19	1 ;	316 204	1*	279 -251		139 -120
1 320 32C	1:	99* 85 111* -70	· "	184 -184 3. La -12		120	*	116* -84	3	102 90	"	277 270	2	288 -30	1	11. 1. 225 -21.	° "'i	13. 1.	12	326 -330 416 407	1 2	14. 1. 3
5 427 -445	1 ***	143 160		129 -106		346 334	2	894 -852	ו 5	549 341 7. L R	2	146 24		1044 -9		214 21	(  ?	219 218		14. 1- *	:	1070 -78
H- 1, L- 1	1.5	113 -72	н•	202 - 206	1	100* -35	:	175 -158	}	203 200 485 -491	°	8. 113	1 2	732 71	3 "	215 -22		1140 -82		314 31A 228 -216		150 -173
3 451 -462	1.0	93• 68	1. 3	1170 -91	H= °	5. 1. 02	H•.	6, 1- 5	1 ;	219 -229	1	174 173	:	768 -78	1	525 53 246 -23	; ;	364 -368		120* 51	:	204 192
7 110 37		110 -77	<b>"</b> :	3. L13 2A8 -292		617 778 638 -638		261 -261	<b>"</b> 1	240 -240	<b>"</b> ?	330 -333	··· !	264 -262	· - '	205 19		130 115	2	600 591 664	<b>"</b> •	212 203
1 179 -207	<b>_</b>	2. L -10	1.3	118 - 02	,	103- 160	*	107 -198	1.3	144 -141	1	1160 -10	2	334 33	_;	155 -14	. ľ	171 -164		144 -129	1.	110 - 179
5 940 -23		273 -272	1	1130 -	1	884 796	1.	916 872	<b>"</b> !	552 564	1.5	131 132		107+ -21	. <b>"</b> !	771 -76		176 -207		136 -104	" e	420
H* 1, L* 8	1.	11239	1.	110* 61	1	565 566		195 200	;	211 207	0	171 175	°;	989 -960		149 -15	(   <del>•</del> .'	13. 1	1.	226 221		146 139
3 676 -705	1	1010 -67	1	3, 115	н <b>,</b>	187 167	×.,	6.1.6	4.	1010 - 10	1	299 -215		245 -22	<b></b>	11		120 -112	1	199 195	۳,	16. 1.
7 330 -323		120* 30 2. L= -11		124 -107	;	1036 -000		92 -91	;	192 192	1	139 -156		131 6	, <u>,</u>	200 -10	, ",	1110 33	;	398 - 194		239 224
1 101 -107 3 622 -656	2	119 108 1040 - 79	2	1314 -1158	;	92 -40	°	106* -103 6, L* -A	"	7. 110	<b>*</b>	9, L• 1 68• -35	2	205 218	1	111 10	;];	254 254		1044 -54	2	172 -167
5 333 327 7 239 -229	H-°	116* 59 2. L= 12	6	489 -509 115 -23	1	*** ****	2	925 -851 599 609		136 141		255 255		10, 1	, ;	315 31 141 -12	;	1044 -42	1.	14. 1 - 11	÷.	110. 57
1 605 -619	1	104* 2		1.5	3	74 34	:	166 -171	[†]	218 201	H. 7	107• 9 9• L• -1	:	258 -261	× 1	11. 1.	1 *	13. 1	'  :	403 396	\$	224 -216
3 371 383 5 1030 -38	11.0	1140 62 2. L+ -12	2	1064 1033		101 120 -47	н.*	1150 95	;	301 382 209 -207	1	87 83 740 49		266 -25		11. L 542 533	1 3	259 263	1.	14. 14 -12 513 503	H.	1170 -26
7 1170 -99		207 -220	1 0	533 544	×.	5. 6- 4	2	349 352	H.	7. 1 11	1 5	88+ -20	1 ***	10, 1+	• j	367 - 36	1 1	121 -105	1 2	354 -360		874 - 17

## Table 3 (cont.)

ĸ	LEOI E C	×	โควไ คว	1 *	FUL FC	1 *	len) er	×	FOI FC	×	ieni ec	×	1F0] Fr	1 *	IFO FC	×	leul et l		1412 40	ĸ	[Full LC	×	leni ro
**	10.1		107+ -110	1 .	1** 1**		115+ 30	1	151 137	1 1	306 - 320	•	116* - 74		20. L12	,	1084 754	7	106* 108		27. 10	H+	24. L+ -10
6	111+ -97	1	120+ -6+	110	17.10	He .	14, 14, 3	•	243 -245	1 ?	101* 15	H•.	20. L2		19] 215		117+ -119		1130 -177	1 1	108* 16	! ?	138 209
۳.,	16. 1.	7   <b>**</b> .	17. 1 2	1 1	114 110	2	218 -192	L	141 -112	1?	12. 1. 20	2	1020 74	1 1	1190 -0	<b>**</b> ,	104 - 40	<b>"</b> 。	144 - 191	· · · '	23. 1 7	h.	24. 111
H-	16. 1	7 3	251 -236	1.5	253 -237	Hr	14.11	1 2	109 292	1	11.8* 12	1 2	109+ 33	He	20. 113	1 5	1094 -158	2	114 276	1	109+ -99	2	119+ 19
÷ 2	113 105	1 5	173 172		17. 19	2	327 300	. 4	116* -79	H.	19. 1+	6	120* 55	2	116* 97	5	1180 101		1144 -157	3	1130 25	H•.	24, 1 - 12
:	108 -54	1 ***.	17. 17	1 1	364 - 354	1 1	207 - 201	<b>"</b> ,	10, 10 -13	1 1	787 299	<b>"</b> ,	20. (* 3	· · · ·	20, 10 -14	<b>**</b> ,	21. 0 -9	<b>~</b> ,	1070 -102	· · ·	23. [ 9	°	25. 1 1
°	16. /		276 -263		105 -169	1 H.	18.1. 4	14	1190 117	1 5	1110 242	14	1190 -05	ž	120+ -9	1 ;	110+ -202		114. 205		1140 -110	1	128 -248
٥	1170 52	·   \$	274 267	на	17. 110	1 0	450 -437		18. 114	140	10.10 -7	He	20. 1 3		71. L. 0	5	119+ 135	•••	22. L8	H.	23. 19	He.	25. L2
2	1100 -70	7	124 -127	1	160 -141	2	397 381	1 3	174 168		249 244	1 2	101+ -101	1	126* 79	I	21. 1 1.		2 3 2 2 2 7		117 198	<b>1</b>	1170 36
	404 -384	°   ° ,	328 -310	3	129 132		18.14	H. *	19.1. 0	1 5	1127		1190 82		224 217	1 ;	112* 135	- 1	115+ 114	н.	23. 1 10	1	151 272
2	944 45	1	726 273	H.	17. 111	0	594 -545	1	109 -107		19. L P		20. 1. 4	. He	71, L* 1	н	21. 111	н.	22. L= -9	1	113+ -159	•	1200 -140
	102+ - 3#		115* - 82	1 1	176 334	1 2	349 344	1 2	348 331	1	103 -106	1 2	256 251	1 1	273 -244		182.9	?	110 151		117* 123	1 **.	2
^°	113		101 100		127 121		1168 - 20	l?	19.19	13	113+ -175	1	20. 1	· ··· '	21. 1	· · · '	21 12	<b></b>	22. 1 10	· .	115* -67		129 245
~~,	46+ -91	ʻ  i	220 -209	H.	17. 112	H.	18, 10 5	1	411 471	He	19, 19	0	347 345	1	774 762	1	1130 69	•	235 -711	j - j	119+ 2	н•	25. 15
4	104+ 21	5	167 165	1	106 - 15	1 2	148 133	1 2	213 -203	1	345 - 370	2	183 -201		1090 -235	1. 3	116+ -131	2	112+ 270	۳.	23. L= -12	1 1	145 -271
<b>.</b> .*	115* 63	·	1190 21	1 2	1190 -50	1*	161 -153	· · · ·	19.11		1150 10		1194 - 10	·?	21. 1. 2	l"",	110 150		22. 1 11		24. 1. 0	'	25. 16
·	166 191	1	106	1.4.	17. 10 -13	2	297 -270	1	362 -367	140	1º. L10	···•	20. 1. 5	1	190 -177	H	21. 114	2	1144 -166	•	198 -199	1	1140 57
2	990 17	6	123 128	1 1	257 -235	1 4	447 422	1 2	176 214	1	101. 04	2	1190 -08	,	152 141	1	1200 -26	···.	27. L12	2	11.80 12		1190 -225
:	112 91	5	1140 - 31	1'	12. 10 -16	1°	18.14	· · · ·	19.1.	1 3	1170 - 107	· **,	1000 47		1010 44	· · ·	404 401		1170 -122	· · · ,	1170 20	· · ·	118 251
۳.	16. 11	1	59+ 34	1.1	11		203 143	1	1044 40	1.44	10, 1= -11	1	1044 -164	1 5	101+ 187	2	312 -303	P.	22. 117	H#	24. L2	1 3	1190 -132
2	117 -57	· 3	95+ 24	1	1184 -53	1 2	242 - 277	1 3	278 -210	1	211 248	•	1164 -96	5	1174 -168	•	118* 65	2	170* 47	2	113+ 78	н.	25. L8
. *	125 98	. 2	352 -330	"*.	17, 10, -15	1 ***	15. 1	·'	118* *2	1 3	1110 -109	<b>"</b>	20. 16	· · · · ·	21. 1. 3	H*,	72. (* 1	۳.	23. 1. 0	· · · 2	1111 - 40		1160 -46
· •	10.0	"   Ha'	17. 1. 5	l'	10. 1. 3	l ž	369 -358	· · ·	201 219	H•'	19. 112	ž	161 200	1 5	1190 -79	1 2	201 222	5	111 -111	2	1140 -24	1	25.1 -9
ž	106* 35	1	191 173	0	635 -624	1 4	720 774	3	116 -128	1	109. 49	•	108+ -31	¥•	21. 6 -3	H-	22.11	144	23.1. 1	•	120+ -137	1	136 -251
4	1130 -80	1	117* -53	2	410 431	*	115* 45	. *	111+ 272	3	1144 94		1194 58	1 1	391 -412	2	115 205	1	112 -114	×-	24. 14	H.	2 10
۳,	16, L -1	<u>۱</u> ۳,	213 -208		1170 -58	۱ <b>۳</b> ,	308 285	· · ·	111 - 100	· · · ·	113* -56	· · · 2	107* -00	1 3	110 -135		22. 1. 2	H.	23. 11	ž	117. 165		25. 111
- 4	1170 -83	i	240 228	He	19 1	i 4	404 - 395	1	101 100	)	1174 #2	4	1090 51	H=	21	0	240 -242	1	169 269	•	1190 -41	1	120* 205
н.	10, 14 -14	4 2	217 -211	2	110 99	. •	543 593		19. 11	H**.	19. 114		120+ 21	11	1160 110	2	170 172		114* -65	۳.,	24.14 -5	<b>**</b>	26. 12
	112	1	17.10.4	1 2	241 239	1			101+ -47		20.1.0	· · ·	101+ 112	· · ·	101 - 45	· · ·	268 - 299	1	1184 -46	1	1194 214	H.	20. 1
H• [*]	16. L -1	5 1	112 22		18. 11	1 2	335 310	÷.	110* +1	0	152 -141	2	103+ -64	j - 5	136 -389	ź	209 377	H.	23.12	H.	24. 16	0	118* -123
2	1190 -45	1.	115* -10	2	294 -250	1 :	207 -203	···.	19, 1- 4	2	1754 48	·*	110+ 41	*	110 83	·*	1150 - 174		120 -186	2	177 261	²	120 226
۳.	910 -61	°  *•,	17, L+ -6	1 3	294 - 282	<b>~</b> °	18.1	;	128 133	[*]	27, 1+ 1	2	105 - 50	1	15 505	2	119+ 82	H. 1	23	1	1190 -30	2	1190 -95
;	354 342	;	273 -257	н.	18. 1. 2	2	130 -147	н.	19.14	2	107* 100	-	112+ 30	3	106* -229	144	22. Le -3	1	1050 -188	He	24. 17	He	26. L6
5	216 -212	1 2	332 308	0	520 505	1 *	251 351	1	431 -454	4	1140 7	P.	20. 110	15	115+ 84	2	10758		113• 91	2	1130 110	1 4	1170 -19
۳.	11	۲L ا	176 -167	1 3	255 250		18. 10 -10		1100 -257	1.	1010 -41		107. 16	1.	1020 54		22. 1	·	108+ 4		24. 1	ו	26. 17
;	263 -257	1.	110 -86		18. 12	0	523 505	н.	19, 1. 5	1 4	110+ 28	1 2	1144 -57	1	131 385	0	351 370	3	1130 -29	0	1120 -146	2	1190 68
. 5	126 125	1.3	120. 57	2	785 747	2	386 - 373	1 1	193 187	1	20. L. 2	H*.	20, L= -11	15	116* -112	1 ?	106 -313	M.	23. 15	2	1140 101	1 **.	26. L8
۲.	17, 1	۱ <b>۳</b> ,		1 2	360 -114	1*	210 211		19. 1	1 3	1100 -90	1 1	1170 37	1	119 -186		22. 15	1	1120 -77	1.	115 13	1 3	1200 174
- ;	109 121	1 3	230 -223		230 22.	1	147 64 -11	1		1.	1101 -10			1 .				1 °		1 *		1.	

#### Description and discussion of the structure

The structure proved to be (III) rather than (II) and the conformation can be seen in Fig. 2. Most bond lengths and angles are shown in Fig. 3. Other distances and angles are listed in Tables 4 and 5, and the weighted mean planes in Table 6. All the given e.s.d.'s were derived from the block-diagonal approximation of the least squares.

# Table 4. Distances and angles involving bonding between the iron atom and the ligand

(a) Distances

Their e.s.d.'s are 0.004-0.005 Å.

$Fe \cdots C(2)$	2·047 Å	$Fe \cdots M(2,3)^*$	1·928 Å
$Fe \cdots C(3)$	2.055	$Fe \cdots M(1,2)$	1.952
$Fe \cdots C(1)$	2.105	$Fe \cdots M(3,4)$	1.957
$Fe \cdots C(4)$	2.108		

*M is the midpoint of the bond between carbon atoms indicated by the numbers.

#### (b) Angles

Their e.s.d.'s are  $0.2-0.3^{\circ}$  except those involving hydrogen atoms whose e.s.d.'s are  $3^{\circ}$ .

C(1)-Fe—C(8)	93·3°	C(2)-FeC(8)	93.3°
C(4)-Fe—C(7)	94·2	C(3)-FeC(7)	91.5
C(1)-Fe—C(9)	100·5	C(2)-FeC(9)	139.5
C(4)-Fe—C(9)	97·6	C(3)-FeC(9)	137.2
C(1)-Fe—C(9)	75·4	C(2)-FeC(3)	39.9
C(1)-FeC(7)	160·0	C(2)-FeC(7)	120·7
C(4)-FeC(8)	162·6	C(3)-FeC(8)	123·9
C(1)-FeC(2)	39·8	C(1)-FeC(3)	69·5
C(3)-FeC(4)	39·9	C(2)-FeC(4)	69·5
FeC(1)-C(2)	67·9	FeC(4)-C(3)	68·1
FeC(1)-C(5')	113·1	FeC(4)-C(5)	112·6
FeC(1)-H(11)	119	FeC(4)-H(4)	120
FeC(2)-C(3)	70·4	FeC(3)-C(2)	69·7
FeC(2)-C(1)	72·3	FeC(3)-C(4)	72·0
FeC(2)-H(21)	120	FeC(3)-H(31)	120

# Table 5. Molecular dimensions of the ligand involving hydrogen atoms

(a) Bond lengths

# Their e.s.d.'s are in the range 0.05-0.08 Å.

C(1) - H(11)	0∙98 Å
C(2) - H(21)	0.92
C(3) - H(31)	0.97
C(4) - H(41)	0.99
C(6)-H(61)	1.00
C(6)-H(62)	0.92

(b) Bond angles

Their e.s.d.'s are in the range 3-5°.

C(5')-C(1)-H(11) C(2) -C(1)-H(11) C(1) -C(2)-H(21) C(3) -C(2)-H(21) C(2) -C(3)-H(31) C(4) -C(3)-H(31)	113° 118 127 117 122 123	C(5)C(6)-H(61) O(1)C(6)-H(61) C(5)C(6)-H(62) O(1)C(6)-H(62) H(61)C(6)-H(62)	114° 106 110 108 110
C(4) - C(3) - H(31)	123		
C(3) - C(4) - H(41) C(5) - C(4) - H(41)	118 112		

This compound can be classified as a cyclic substituted butadiene complex. The bonding between the iron atom and the butadiene group is not yet fully understood (e.g. see Churchill & Mason, 1967a; Green, 1968) even though several such structures have been determined by X-ray diffraction (Dickens & Lipscomb, 1962; Smith & Dahl, 1962; Dodge, 1964; Bailey & Mason, 1966; Churchill & Mason, 1967b; Robson & Truter, 1968; Paul, Johnson, Paquette, Barrett & Haluska, 1968; Birch, Fitton, McPartlin & Mason, 1968; Beddoes, Lindley & Mills, 1970). The geometry of the butadiene-irontricarbonyl moiety is similar to that observed in previous analyses. However, since the present determination is more accurate than those referred to before, these results may contribute to the understanding of the Fe-ligand bonding of these complexes.

As is usual in these complexes, the conformation of the ligand, or part of it, is dictated by the bonding to the irontricarbonyl groups. The tricyclic ligand has

#### Table 6. Weighted least-squares planes

Plane 1		Plane 2		Р	lane 3	Pla	ine 4	Plane 5		
O(1) C(5) C(5') C(6) C(6')	⊿ 0.000 Å 0.002 -0.002 -0.002 0.002	C(1) C(2) C(3) C(4) H(21) H(31) H(11)* H(41)* C(5)* C(5')* Fe*	$\begin{array}{c} \varDelta \\ 0.000 \text{ Å} \\ 0.000 \\ - 0.003 \\ 0.001 \\ 0.106 \\ 0.113 \\ 0.157 \\ 0.157 \\ 0.150 \\ - 0.977 \\ - 0.986 \\ 1.643 \end{array}$	C(1) C(4) C(5) C(5')	⊿ 0.003 Å -0.003 0.005 -0.005	C(1) C(4) C(7) C(8) O(2)* O(3)* Fe* C(9)* O(4)* M(2,3)*	$\begin{array}{c} 4 \\ - 0.023 \text{ \AA} \\ 0.022 \\ - 0.034 \\ 0.038 \\ - 0.253 \\ - 0.112 \\ 0.278 \\ 2.067 \\ 3.191 \\ - 1.217 \end{array}$	C(7) C(8) C(9) Fe* O(2)* O(3)* O(4)*	⊿ 0.0 Å 0.0 0.920 0.568 0.571 0.622	
r.m.s	d. = 0.002 $\ell^2 = 0.6$	r.m.s.d $\chi^2 =$	1. = 0.063 8.9	r.m.s. X	d. = 0.004 $d^2 = 3.3$	r.m.s.d. $\chi^2 =$	=0.030 130.1	r.m.: X	s.d. = $0.0$ $^{2} = 0.0$	

* 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(Å)	<i>k</i> (Å)	<i>l</i> (Å)	<i>m</i> (Å)
1:	<b>20</b> ·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	0.012	1.387
5:	18.712	3.127	-4.091	3.151

Some dihedral angles between the planes

∠1,2	∠1,3	∠2,3	∠1,4	∠2,4	∠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  $C_{sp3}$ - $C_{sp3}$  and for  $C_{sp3}$ - $C_{sp2}$ 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  $\Delta l/\sigma(\Delta l)$ 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 $\cdots$ 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,  $Fe \cdots M(2,3)$  [1.928 (5) Å] being shorter than the average [1.955 (3) Å] of the two equal  $Fe \cdots M(1,2)$  and  $Fe \cdots M(3,4)$  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  $(U=0.1641 \text{ Å}^2)$  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  $1.426 \pm 0.005$  Å given by Sutton (1965).

The irontricarbonyl 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 irontricarbonyl 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.

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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.

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

# By J. Krogh-Moe

Chemistry Department, University of Trondheim, Trondheim, Norway

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The high-temperature modification of potassium pentaborate,  $\alpha$ -K₂O.5B₂O₃, 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 BO₃ 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,  $\beta$ -K₂O.5B₂O₃, 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  $\varrho_{\beta}/\varrho_{x} = 1.19$ ), 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  $\alpha$ -K₂O. 5B₂O₃ 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 × 0.0095 × 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. Unitcell 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 K₂O.5B₂O₃ in the cell, the calculated density is 1.93 g.cm⁻³. Krogh-Moe (1959b) 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  $62.9 \text{ cm}^{-1}$ , 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-