

The Crystal Structure of Iron Cupferron $\text{Fe}(\text{O}_2\text{N}_2\text{C}_6\text{H}_5)_3^*$

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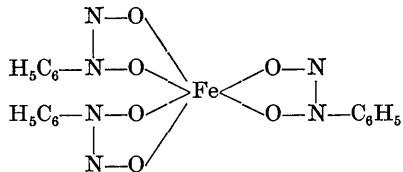
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The structure of iron cupferron, $\text{Fe}(\text{O}_2\text{N}_2\text{C}_6\text{H}_5)_3$, has been determined by three-dimensional Fourier and least-squares methods. The crystals are monoclinic with the unit-cell dimensions $a_0 = 12.50$, $b_0 = 17.45$, $c_0 = 11.15 \text{ \AA}$; $\beta = 122^\circ 19'$. There are four molecules per unit cell and the space group is $P2_1/a$. The three cupferron groups are unsymmetrically attached to the iron ion, and therefore crystallographically independent. The iron–oxygen bonding seems to be ionic.

Introduction

The crystal structure of tri-(*N*-nitrosophenylhydroxylamine)iron(III), *i.e.* iron cupferron,



is one of several investigations carried out in this laboratory on chelates. In strongly acidified solutions, cupferron precipitates a great number of ions, such as cerium(IV), niobium, gallium, iron, tantalum, tin(IV), titanium, tungsten, uranium(IV), vanadium, and zirconium; and in less acidic media some like aluminum, bismuth, cerium(III), copper, lead, mercury, silver, and thorium.

Preliminary structure investigations of uranylcupferrates were made by Horton (1956). Neumann, Lundgren & Aurvillius (1956) have carried out structural investigations on $\text{Zr}(\text{C}_6\text{H}_5\text{N}_2\text{O}_2)_4$, and the iso-morphous Hf and Hf-Zr (1:1) compounds, which crystallize in the space group $Pbcn$.

Experimental

A precipitate of iron cupferron was prepared by the method of Flagg (1948). The spongy precipitate was recrystallized from ether. The slowly grown crystals were garnet red and formed parallelepiped-shaped plates. Under the polarizing microscope the extinctions of a crystal, resting on its plate face, are oblique,

while on all other faces, after 90° rotation from the plate face, only straight extinctions are observed. The crystals are therefore probably monoclinic.

The parameters of the unit cell were determined by interpolation of the positions of several reflections with a crystal sprinkled with some sodium chloride powder ($a = 5.639 \text{ \AA}$). Iron radiation was used throughout ($\lambda(K\alpha) = 1.936 \text{ \AA}$). The parameters of the unit cell are

$$a_0 = 12.50 \pm 0.01, \quad b_0 = 17.45 \pm 0.05, \\ c_0 = 11.15 \pm 0.04 \text{ \AA}; \quad \beta = 122^\circ 19' \pm 5'.$$

The density was measured by the flotation method as 1.50, which gives 4·1, *i.e.* 4 molecules per unit cell. A weight analysis gave an experimental value of 11.96% iron, against a theoretical value of 11.95%.

Systematic extinctions were observed for $h0l$ when $h \neq 2n$, and for $0k0$ when $k \neq 2n$. The space group was determined as $P2_1/a$.

A crystal was ground to a cylinder with a radius of 0.3 mm, and a length of 0.3 mm. The crystal was mounted on the axis of the cylinder which coincides with the b axis of the unit cell. With this crystal eight layers of Weissenberg pictures were taken, which yielded 1510 relative intensities. An additional 200 relative intensities with $k > 7$ were observed from three layers of Weissenberg pictures around the c axis. The intensities were corrected in the usual way, but no correction for absorption was made.

Determination of the trial structure and refinement

A more detailed description of the determination and refinement of the structure has been given elsewhere (van der Helm, 1960). All calculations were three-dimensional.

A sharpened Patterson synthesis yielded the positions of the iron atom and the six oxygen atoms. The oxygen atoms formed a distorted octahedron

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Table 1. Structure factors of iron cupferron

The star indicates an unobserved reflection. The listed value of F_0 for those reflections is half of the minimal structure factor amplitude which is observable at the position of the reflection

k	l	r_o	r_c																					
0	0	261	315	6	5	375	326	17	1	111	146*	*1	7	16	33	10	2	120	130	3	10	96	90*	
2	0	924	1504*	11	0	247	236*	6	5	279	200	2	7	155	279	11	2	94	93	4	10	217	213*	
4	0	1291	1873	5	2	225	187	7	5	175	120	0	2	1113	1462*	2	7	12	66	10	5	10	113	82
6	0	466	667*	13	0	321	312	7	5	61	71	0	2	108	76	3	7	289	264*	12	2	455	443	
8	0	291	295	15	0	184	168*	8	5	163	181	1	2	161	163	12	2	211	234*	6	10	60	38	
10	0	122	75	13	0	146	120*	9	5	110	77	*1	2	91	39	4	7	223	186*	0	5	459	336	
12	0	146	171	14	0	146	171	2	2	715	616	4	7	442	362	13	2	118	162*	0	5	461	350*	
1	1	1208	1580*	17	0	181	191	*1	6	18	10	2	2	715	616	14	2	211	234*	1	0	21	34	
2	1	313	352*	1	1	231	246*	1	6	205	215*	3	2	117	119*	5	7	21	15	2	0	258	237	
3	1	36	51*	1	1	231	246*	2	6	21	10	3	2	117	119*	6	7	267	248*	15	2	127	121	
4	1	791	1161	1	1	20	70	4	2	20	71	4	2	1225	1290	6	7	286	215*	7	1	300	203	
5	1	200	291	2	1	31	43	1	0	305	276	4	2	365	319	7	7	223	195	5	0	599	559	
6	1	293	331	3	1	47	47	1	0	216	194	5	2	119	130	6	2	190	152*	4	0	962	902*	
7	1	261	283	3	1	301	296*	6	6	33	11	5	2	728	695	8	7	89	137*	6	0	382	318	
8	1	10	66	1	1	277	247	6	6	29	9	6	2	113	68	6	7	13	2	1	350	301*		
9	1	421	552	1	1	66	756	5	6	235	210	*6	2	51	71	1	0	21	238*	5	5	27	37	
10	1	118	117	5	1	131	131	6	6	157	156	7	2	153	153	0	8	233	151	6	0	150	143*	
11	1	109	100	5	1	131	131	7	6	157	156	8	2	153	153	12	0	204	154	7	0	203	190	
12	1	88	89	5	1	131	131	8	6	108	282	8	2	153	153	13	0	187	154	8	0	190	140*	
0	2	1322	1472*	6	1	165	216	7	6	161	163	9	2	134	167	2	8	166	165	4	3	208	231	
1	2	255	238*	*7	1	8	68	8	6	92	68	8	2	214	252	2	8	152	151	5	2	252	259*	
2	2	676	605	7	1	76	77	8	2	270	218	10	2	61	60	3	8	47	14	5	3	208	231	
3	2	607	570	8	1	196	241	9	2	210	234	10	2	510	501	3	8	351	202	5	2	604	690	
4	2	528	494	8	1	322	340	*1	7	18	1	11	214	144	4	8	202	230	1	0	195	201		
5	2	384	343	9	1	133	133	1	7	106	85	11	2	237	321	5	3	175	175	1	0	195	201	
6	2	452	494*	10	1	231	249	7	6	161	163	12	2	237	311	5	3	167	167	5	2	163	159	
7	2	180	180	11	1	270	271	7	6	108	107	12	2	237	311	5	3	167	167	5	2	240	240*	
8	2	539	511*	12	1	68	72	8	2	166	166	13	2	214	214	5	3	199	211	3	2	351	344	
9	2	627	612	13	1	218	210	3	7	90	81	13	2	61	61	3	1	189	187	4	2	297	297	
10	2	722	614	11	1	211	181	4	7	29	52	14	2	169	160	6	3	177	177	4	1	206	201	
11	2	65	10	15	1	310	318	5	7	177	155	15	2	169	160	6	3	177	177	9	2	209	238	
12	2	65	76	16	1	431	354	5	7	167	222	15	2	153	151	0	9	161	163	5	0	195	201	
13	2	103	135	13	1	91	39	5	7	57	8	16	2	153	151	1	0	181	181	5	2	126	132	
14	2	63	134	14	1	375	411	6	7	115	145	16	2	219	196	2	9	162	192	10	2	284	309	
15	2	114	116	14	1	234	234	6	7	141	169	16	2	166	165	6	6	115	166	10	2	72	93	
16	2	111	88	15	1	103	127	7	7	28	33	17	0	205	225	6	6	106	106	11	2	297	193*	
17	2	109	99	16	1	248	248	7	7	170	200	0	3	180	205	5	6	208	212	13	2	207	211	
0	3	243	244	16	1	238	248	8	7	16	9	1	1	710	611	6	6	127	127	15	2	114	117*	
1	3	329	323	9	1	112	118	*1	6	112	118	1	1	192	118	6	6	122	122	15	2	126	132	
2	3	207	194	1	2	90	1076	1	8	1	74	41	2	167	229	0	10	189	237	1	0	186	157*	
3	3	314	294	2	2	176	224	2	8	21	71	3	1	111	292	0	10	189	237	1	0	186	157*	
4	3	341	320	2	2	172	214	3	9	94	78	3	3	366	251	2	10	120	100	2	6	251	226*	
5	3	535	500	2	2	101	96	3	10	109	119	4	3	102	119	2	6	107	107	3	2	291	268*	
6	3	621	586	3	2	91	92	4	7	93	75	5	3	709	615	3	6	107	81	3	2	322	227	
7	3	1	21	4	2	628	689	4	8	51	51	5	3	318	267	1	5	101	123	1	3	127	83*	
8	4	102	113	5	2	121	67	5	8	113	125	6	1	531	507	0	11	21	55	1	3	50	66	
9	4	127	111	5	2	186	180	6	8	186	225	7	3	111	266	4	2	221	234	2	3	234	227	
10	4	111	111	6	2	242	242	7	3	111	266	12	0	221	234	5	2	177	177	3	3	285	267*	
11	4	23	42	6	2	238	254	7	3	111	268	13	0	167	195	5	2	166	166	4	3	305	287*	
12	4	716	616	6	2	242	242	8	3	108	104	14	0	167	195	5	2	166	166	4	3	305	287*	
13	4	166	166	7	2	104	68	6	4	248	312	15	0	168	188	8	2	166	166	4	3	305	287*	
14	5	267	265	8	2	104	119	7	4	248	312	16	0	168	188	8	2	166	166	4	3	305	287*	
15	6	237	237	1	3	260	261	0	0	168	188	17	0	247	276	7	1	204	211	1	4	111	35*	
16	6	270	245*	1	3	210	304	0	0	168	188	18	0	247	276	7	1	204	211	1	4	111	35*	
17	6	245	245	2	3	304	304	0	0	168	188	19	0	247	276	7	1	204	211	1	4	111	35*	
18	6	245	245	2	3	311	183	0	0	168	188	20	0	247	276	7	1	204	211	1	4	111	35*	
19	6	257	257	3	1	309	280	0	0	167	180	21	0	247	276	7	1	204	211	1	4	111	35*	
20	6	217	212	3	1	202	197	0	0	167	180	22	0	247	276	7	1	204	211	1	4	111	35*	
21	6	82	90	3	1	217	212	0	0	167	180	23	0	247	276	7	1	204	211	1	4	111	35*	
22	7	261	243	4	1	220	220	0	0	167	180	24	0	247	276	7	1	204	211	1	4	111	35*	
23	7	133	132	5	2	357	402	0	0	168	180	25	0	247	276	7	1	204	211	1	4	111	35*	
24	7	378	361	5	3	527	573	0	0	168	180	26	0	247	276	7	1	204	211	1	4	111	35*	
25	7	86	87	6	3	517	563	0	0	168	180	27	0	247	276	7	1	204	211	1	4	111	35*	
26	7	87	87																					

Table 1 (cont.)

k 1	F _o	F _c	k 1	F _o	F _c	k 1	F _o	F _c	k 1	F _o	F _c	k 1	F _o	F _c	k 1	F _o	F _c	k 1	F _o	F _c	k 1	F _o	F _c			
1 8 -	125	67	15 2 -	104	100	8 9 -	21	67	1 4 -	207	204	4 1 -	502	493	9 7 -	20	26	2 4 -	164	190	0 3 -	478	386	8 7 -	12	15
2 3 7 -	128	129	0 3 -	159	149	0 10 -	159	126	1 2 5 -	129	123	5 3 4 -	19	19	3 4 -	97	93	1 2 5 -	105	105	0 2 -	212	197	8 6 -	116	108
3 5 6 -	129	276	0 3 -	152	357	1 10 -	120	124	2 2 4 -	127	86	5 1 -	116	121	0 8 -	349	348	2 2 4 -	112	107	1 2 -	272	229	8 5 -	119	109
4 6 7 -	125	323	1 3 -	370	357	2 10 -	225	221	3 3 4 -	19	91	6 1 -	110	117	1 2 5 -	104	72	3 2 -	212	197	1 2 -	128	117	8 4 -	126	117
5 7 8 -	172	153	2 2 -	31	63	3 10 -	370	310	4 3 4 -	19	92	6 1 -	117	127	7 1 -	357	359	3 2 -	19	57	0 5 -	123	137	8 3 -	126	114
6 8 9 -	172	153	3 3 -	807	828	5 10 -	70	76	5 1 -	232	227	6 1 -	159	152	7 1 -	155	165	6 1 -	153	142	6 3 -	166	153	7 2 -	27	27
7 9 10 -	244	285	4 3 -	363	377	7 10 -	62	69	8 1 -	232	227	1 2 5 -	167	166	6 1 -	159	152	1 2 5 -	167	166	0 6 -	247	232	8 5 -	92	82
8 10 11 -	119	157	5 3 -	320	320	9 11 -	271	302	8 1 -	277	274	1 1 -	159	149	9 1 -	155	151	1 2 5 -	167	166	1 2 -	217	206	8 4 -	117	117
9 12 13 -	198	182	6 3 -	15	18	2 11 -	106	39	8 1 -	261	254	1 1 -	159	163	0 2 -	215	226	7 8 -	169	193	0 5 -	205	224	8 3 -	65	65
10 12 14 -	239	180	7 3 -	550	477	3 13 -	113	115	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 6 -	157	157	8 5 -	107	107
11 12 15 -	20	17	8 3 -	19	47	4 11 -	115	47	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 7 -	156	156	8 6 -	66	66
12 13 16 -	19	15	9 3 -	7	7	5 11 -	78	265	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 8 -	156	156	8 7 -	76	76
13 14 17 -	15	1	10 3 -	32	265	6 10 -	62	69	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 9 -	156	156	8 8 -	75	75
1 10 -	96	158	8 3 -	7	16	11 10 -	7	7	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 10 -	227	214	8 9 -	20	20
2 10 -	152	96	9 3 -	15	15	12 10 -	120	128	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 11 -	156	156	8 10 -	25	25
3 10 -	211	217	0 4 -	370	322	13 10 -	50	55	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 12 -	156	156	8 11 -	17	17
4 10 -	231	217	1 4 -	583	528	14 10 -	50	55	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 13 -	156	156	8 12 -	15	15
5 10 -	12	2	2 2 -	26	26	15 10 -	6	9	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 14 -	257	249	8 13 -	12	12
6 10 -	12	2	2 2 -	27	201	16 10 -	7	10	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 15 -	156	156	8 14 -	21	21
7 10 -	12	2	2 2 -	165	165	17 10 -	8	16	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 16 -	156	156	8 15 -	15	15
8 11 -	78	57	1 1 -	310	289	18 10 -	10	12	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 17 -	156	156	8 16 -	15	15
9 11 -	115	112	1 1 -	510	510	19 10 -	12	12	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 18 -	156	156	8 17 -	15	15
10 11 -	155	138	1 1 -	435	367	20 10 -	13	0	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 19 -	156	156	8 20 -	15	15
11 12 -	156	156	1 1 -	239	239	21 10 -	1	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 20 -	156	156	8 21 -	15	15
12 13 -	152	151	1 1 -	284	284	22 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 21 -	156	156	8 22 -	15	15
13 14 -	152	151	1 1 -	284	284	23 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 22 -	156	156	8 23 -	15	15
14 15 -	156	156	1 1 -	284	284	24 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 23 -	156	156	8 24 -	15	15
15 16 -	156	156	1 1 -	284	284	25 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 24 -	156	156	8 25 -	15	15
16 17 -	156	156	1 1 -	284	284	26 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 25 -	156	156	8 26 -	15	15
17 18 -	156	156	1 1 -	284	284	27 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 26 -	156	156	8 27 -	15	15
18 19 -	156	156	1 1 -	284	284	28 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 27 -	156	156	8 28 -	15	15
19 20 -	156	156	1 1 -	284	284	29 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 28 -	156	156	8 29 -	15	15
20 21 -	156	156	1 1 -	284	284	30 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 29 -	156	156	8 30 -	15	15
21 22 -	156	156	1 1 -	284	284	31 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 30 -	156	156	8 31 -	15	15
22 23 -	156	156	1 1 -	284	284	32 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 31 -	156	156	8 32 -	15	15
23 24 -	156	156	1 1 -	284	284	33 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 32 -	156	156	8 33 -	15	15
24 25 -	156	156	1 1 -	284	284	34 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 33 -	156	156	8 34 -	15	15
25 26 -	156	156	1 1 -	284	284	35 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 34 -	156	156	8 35 -	15	15
26 27 -	156	156	1 1 -	284	284	36 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 35 -	156	156	8 36 -	15	15
27 28 -	156	156	1 1 -	284	284	37 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 36 -	156	156	8 37 -	15	15
28 29 -	156	156	1 1 -	284	284	38 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 37 -	156	156	8 38 -	15	15
29 30 -	156	156	1 1 -	284	284	39 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 38 -	156	156	8 39 -	15	15
30 31 -	156	156	1 1 -	284	284	40 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 39 -	156	156	8 40 -	15	15
31 32 -	156	156	1 1 -	284	284	41 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 40 -	156	156	8 41 -	15	15
32 33 -	156	156	1 1 -	284	284	42 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 41 -	156	156	8 42 -	15	15
33 34 -	156	156	1 1 -	284	284	43 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 42 -	156	156	8 43 -	15	15
34 35 -	156	156	1 1 -	284	284	44 10 -	2	1	1 2 5 -	159	152	1 2 5 -	167	166	8 1 -	155	151	1 2 5 -	167	166	0 43 -	156	156	8 44 -	15	

(1957) was used to obtain coordinate shifts from the plotted x - y and x - z sections of the difference Fourier syntheses. The exact values of the temperature factor corrections were not used in the consecutive refinement cycles, but rather an average adjustment was made for each type of atom by using the information from individual corrections. There were indications of several hydrogen atoms in the third difference Fourier synthesis. Calculated hydrogen positions were used for a last structure factor calculation ($R=0.15$), from which a final Fourier synthesis was calculated. Figs. 1, 2, 3 and 4 show comparable drawings of

sections of the last Fourier synthesis and the last difference Fourier synthesis. The following two features made it doubtful that further refinement would be useful with the present data. Many atoms like O(4) and O(6) (Fig. 1) showed non-spherical electron density. This was caused by absorption rather than by anisotropic temperature movement because the positions of the ellipsoids with respect to the crystallographic axes were in all cases similar. The second feature was the high temperature factors of some of the carbon atoms (C(15) and C(16) in Fig. 3). A discussion of this last observation will follow. The final calculated and observed structure factors appear in Table 1. Final parameters are given in Table 2.

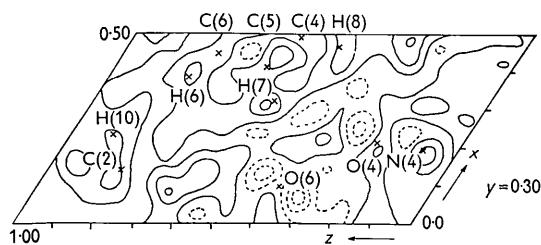


Fig. 1. Final difference Fourier synthesis at $y = 0.30$. Contours are at intervals of $0.2 \text{ e.}\text{\AA}^{-3}$.

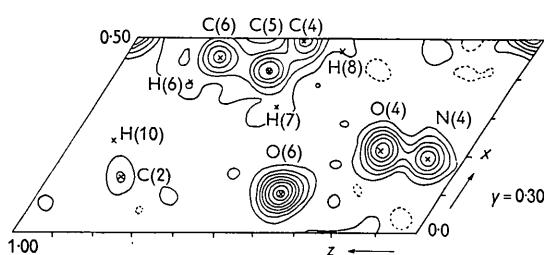


Fig. 2. Final Fourier synthesis at $y = 0.30$. Contours are at intervals of $1.0 \text{ e.}\text{\AA}^{-3}$.

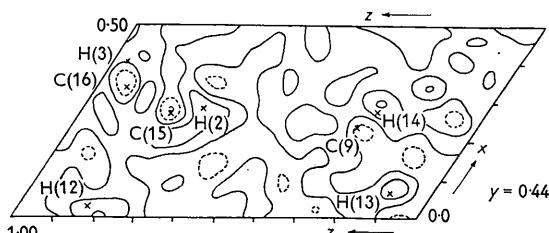


Fig. 3. Final difference Fourier synthesis at $y = 0.44$. Contours are at intervals of $0.2 \text{ e.}\text{\AA}^{-3}$.

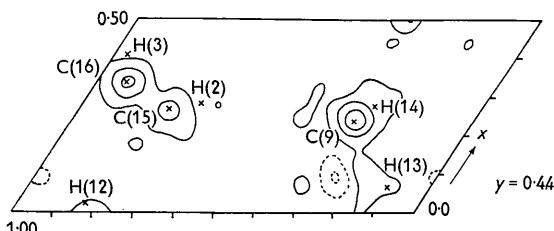


Fig. 4. Final Fourier synthesis at $y = 0.44$. Contours are at intervals of $1.0 \text{ e.}\text{\AA}^{-3}$.

Table 2. Final coordinates and temperature factor coefficients

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Fe	0.079	0.236	0.241	2.15
O(1)	0.034	0.202	0.049	3.55
O(2)	0.209	0.169	0.397	3.55
O(3)	0.939	0.312	0.145	3.55
O(4)	0.216	0.280	0.219	3.55
O(5)	0.980	0.146	0.243	3.55
O(6)	0.102	0.305	0.396	3.55
N(1)	0.101	0.238	0.005	3.65
N(2)	0.159	0.113	0.430	3.65
N(3)	0.934	0.360	0.232	3.65
N(4)	0.197	0.281	0.091	3.65
N(5)	0.038	0.097	0.350	3.65
N(6)	0.021	0.360	0.366	3.65
C(1)	0.070	0.229	0.863	4.10
C(2)	0.150	0.255	0.821	4.10
C(3)	0.114	0.246	0.681	4.10
C(4)	0.998	0.213	0.585	4.10
C(5)	0.917	0.191	0.623	4.10
C(6)	0.954	0.196	0.769	4.10
C(7)	0.235	0.067	0.553	4.10
C(8)	0.186	0.004	0.580	4.10
C(9)	0.262	0.963	0.706	4.10
C(10)	0.383	0.988	0.800	4.10
C(11)	0.431	0.049	0.773	4.10
C(12)	0.358	0.093	0.647	4.10
C(13)	0.839	0.420	0.179	4.10
C(14)	0.825	0.464	0.276	4.10
C(15)	0.732	0.522	0.222	4.10
C(16)	0.662	0.534	0.073	4.10
C(17)	0.678	0.491	0.983	4.10
C(18)	0.769	0.431	0.035	4.10

Computation

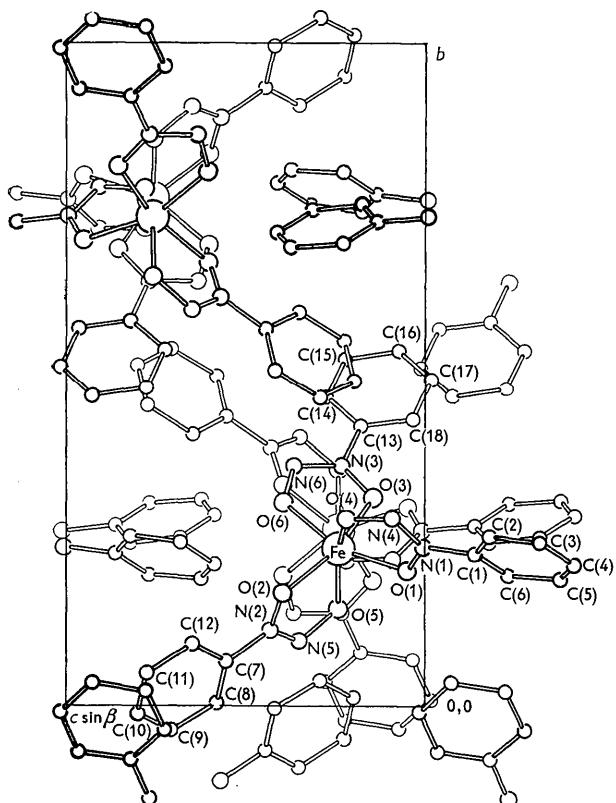
All computations were made on an IBM 650 electronic computer, equipped with magnetic tapes. The programs used in the present analysis, Fourier summation, structure-factor and least-squares calculations, were reported by two of us (Merritt & van der Helm, 1959). The scattering factors for carbon, nitrogen, and oxygen were the values given by McWeeny (1951), while the Thomas-Fermi curve was used for the scattering factor of iron. Because of the anomalous absorption of iron radiation by iron, 2.37 was subtracted from these values throughout the whole range of $\sin \theta/\lambda$.

Table 3. Bond distances

					Average
Fe-O(1)	1.99 Å	Fe-O(2)	2.00 Å	Fe-O(3)	1.99 Å
Fe-O(4)	2.01	Fe-O(5)	2.01	Fe-O(6)	2.00
O(1)-N(1)	1.33	O(2)-N(2)	1.31	O(3)-N(3)	1.31
O(4)-N(4)	1.32	O(5)-N(5)	1.32	O(6)-N(6)	1.30
N(1)-N(4)	1.30	N(2)-N(5)	1.31	N(3)-N(6)	1.30
C(1)-N(1)	1.42	C(7)-N(2)	1.43	C(13)-N(3)	1.45
C(1)-C(2)	1.39	C(7)-C(8)	1.37	C(13)-C(14)	1.41
C(2)-C(3)	1.38	C(8)-C(9)	1.40	C(14)-C(15)	1.41
C(3)-C(4)	1.39	C(9)-C(10)	1.37	C(15)-C(16)	1.42
C(4)-C(5)	1.35	C(10)-C(11)	1.33	C(16)-C(17)	1.35
C(5)-C(6)	1.44	C(11)-C(12)	1.42	C(17)-C(18)	1.42
C(6)-C(1)	1.38	C(12)-C(7)	1.40	C(18)-C(13)	1.37

Table 4. Bond angles

				Average	
O(1)FeO(4)	75.6°	O(2)FeO(5)	75.6°	O(3)FeO(6)	75.0°
FeO(1)N(1)	112.5	FeO(2)N(2)	113.0	FeO(3)N(3)	113.9
FeO(4)N(4)	117.8	FeO(5)N(5)	118.9	FeO(6)N(6)	119.3
O(1)N(1)N(4)	120.9	O(2)N(2)N(5)	121.3	O(3)N(3)N(6)	120.9
O(4)N(4)N(1)	110.6	O(5)N(5)N(2)	110.7	O(6)N(6)N(3)	110.8
O(1)N(1)C(1)	119.8	O(2)N(2)C(7)	120.1	O(3)N(3)C(13)	119.9
N(4)N(1)C(1)	117.8	N(5)N(2)C(7)	117.9	N(6)N(3)C(13)	118.0
N(1)C(1)C(2)	116.0	N(2)C(7)C(8)	115.7	N(3)C(13)C(14)	116.7
N(1)C(1)C(6)	121.5	N(2)C(7)C(12)	120.8	N(3)C(13)C(18)	119.3
C(6)C(1)C(2)	122.3	C(12)C(7)C(8)	122.6	C(18)C(13)C(14)	123.9
C(1)C(2)C(3)	119.1	C(7)C(8)C(9)	119.2	C(13)C(14)C(15)	118.3
C(2)C(3)C(4)	119.7	C(8)C(9)C(10)	119.0	C(14)C(15)C(16)	117.2
C(3)C(4)C(5)	121.9	C(9)C(10)C(11)	121.7	C(15)C(16)C(17)	122.9
C(4)C(5)C(6)	119.9	C(10)C(11)C(12)	121.7	C(16)C(17)C(18)	120.6
C(5)C(6)C(1)	117.1	C(11)C(12)C(7)	115.7	C(17)C(18)C(13)	116.8

Fig. 5. Projection of the structure of iron cupferron viewed along the a axis.

Description and discussion of the structure

The contents of roughly one unit cell are shown in Fig. 5. The view is along the a axis. The coordinates of the numbered molecule are the ones given in Table 2.

The bond lengths and bond angles are given in Tables 3 and 4. The method of Cruickshank (1949) was used to calculate the standard deviations of the coordinates which are given in Table 5. From these values the maximum and minimum standard deviations of the bond lengths are calculated (Table 6). The maximum value applies to a bond parallel to the z axis, while the minimum value belongs to a bond which is parallel to the $x-y$ plane. Because the coordinates of the carbon atoms were refined

Table 5. Standard deviation of coordinates

	σ_x	σ_y	σ_z
C	0.010 Å	0.011 Å	0.019 Å
N	0.007	0.009	0.014
O	0.006	0.007	0.011
Fe	0.001	0.002	0.003

Table 6. Minimum and maximum standard deviations of bond lengths

Bond type	Min. s.d.	Max. s.d.
C-C	0.015 Å	0.026 Å
C-N	0.013	0.023
N-N	0.011	0.019
N-O	0.010	0.018
Fe-O	0.007	0.011

Table 7. Least-squares planes: $Rx + Sy + Tz = d$

Atoms	Plane				
	R	S	T	d	
C(1)C(2)C(3)C(4)C(5)C(6)	-4.748	16.024	0.351	3.29	(A)
C(7)C(8)C(9)C(10)C(11)C(12)	-8.926	10.656	8.797	3.48	(B)
C(13)C(14)C(15)C(16)C(17)C(18)	9.905	11.863	-3.851	2.70	(C)
O(1)N(1)N(4)O(4)C(1)	-7.035	14.298	0.825	2.69	(D)
O(2)N(2)N(5)O(5)C(7)	-7.220	11.553	8.864	3.97	(E)
O(3)N(6)N(6)O(6)C(13)	10.188	11.399	-6.261	2.02	(F)

Table 8. Deviation from least-squares planes

(Å × 10⁻³)

A	D	B	E	C	F
C(1)	-5	-17	C(7)	-2	+10
C(2)	+17	-242	C(8)	+2	-125
C(3)	-6	-233	C(9)	-5	-30
C(4)	-17	+32	C(10)	+8	+218
C(5)	+28	+319	C(11)	-8	+337
C(6)	-16	+250	C(12)	+4	+256
O(1)	+4	O(2)	+6	O(3)	+10
O(4)	-21	O(5)	+16	O(6)	+8
N(1)	+11	N(2)	0	N(3)	-38
N(4)	+22	N(5)	-20	N(6)	+3

while using the same temperature factor for all of them where they actually differ considerably in their temperature movement, it is assumed that the standard deviation in the bond distances of the phenyl rings is more safely estimated as being between 0.03 Å and 0.04 Å. The standard deviation of the bond angle O-Fe-O is 20', and of an angle in a phenyl ring 56'.

Least-squares planes were calculated for each of the phenyl rings and for planes through the atoms O(1)N(1)N(4)O(4)C(1), O(2)N(2)N(5)O(5)C(7) and O(3)N(3)N(6)O(6)C(13) (Schomaker, Waser, Marsh & Bergman, 1959). The results are tabulated in Table 7, while deviations from the least-squares planes are given in Table 8. The phenyl rings are flat within the limits of observation, but are not coplanar with the nitrosohydroxylamino group to which they are attached. The angle between them is of the order of 10°. The deformation from coplanarity consists mainly of a rotation of the phenyl groups around the N-C bonds in addition to non-planarity of the $\text{N}=\text{O}-\text{N}-\text{C}$ bonding system. This can be seen from deviations given in Table 8.

The three cupferron groups in the molecule $\text{NH}_4[\text{UO}_2(\text{C}_6\text{H}_5\text{N}_2\text{O}_2)_3]$ are related by a threefold axis (Horton, 1956). In the molecule of iron cupferron there is one possible direction for a threefold axis, which is (Fig. 5): center of mass O(2)O(4)O(6)-Fe-center of mass O(1)O(3)O(5), close to the [101] direction. Fig. 6 shows one molecule viewed along the [101] direction. It is clear that the oxygen atoms depart considerably from the symmetry 32 of the regular octahedron. One can expect statistically 75% *trans* (1,2,6) and 25% *cis* (1,2,3) in the formation of a chelate with three unsymmetrical bidentate ligands.

It is evident from Fig. 6 that the molecule shown is *trans* (or unsymmetrical) because two phenyl groups are attached to the 'lower' nitrogen while one phenyl group (*B*) is attached to the 'higher' nitrogen atom of the respective nitrosohydroxylamino groups. There is only one molecule in the asymmetric unit and the crystal consists therefore entirely of *trans* molecules.

All coordinates of one molecule are independent of each other. The similarity in bond lengths and angles in the three cupferron groups is evident from Tables 3 and 4, which also show that the irregularities in

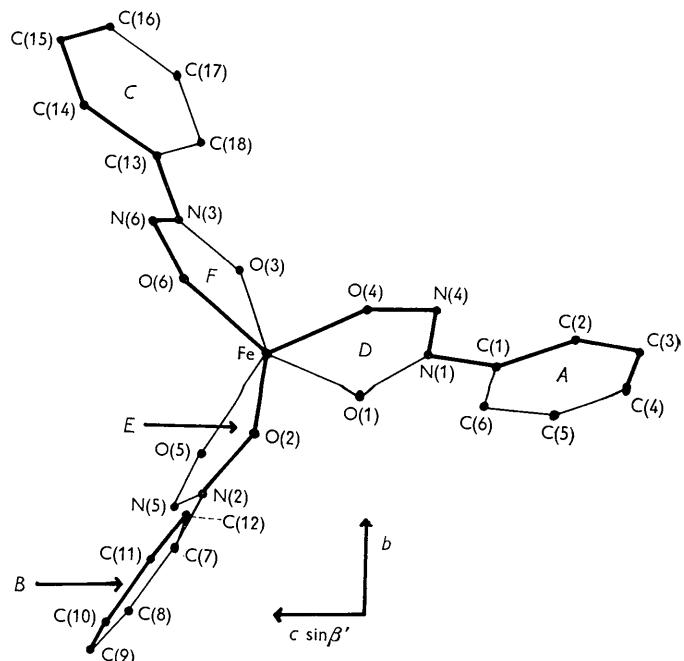


Fig. 6. A view of the molecule along the [101] direction.

the phenyl groups are to a large extent similar. It seems therefore, useful to calculate an average cupferron group which is presented in Fig. 7.

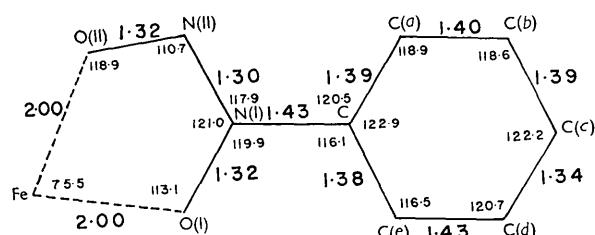


Fig. 7. The cupferron group. Bond distances and angles are average values from the three crystallographically independent cupferron groups (compare Tables 3 and 4).

Because the irregularities occur in each of the three phenyl groups they appear to be relevant. A thorough investigation into the irregularity of bond distances in phenyl rings is being made by Kennard (1960). One of her conclusions, kindly relayed to us before publication, is the strong suggestion that the apparent scatter of bond distances is related to anisotropic movements of atoms in and near the phenyl group. Theoretical consideration of the relation between bond distance and anisotropic motion has been given by Cruickshank (1956, 1961).

A closer examination of the temperature movements of the carbon atoms was made. A qualitative conclusion from the last difference Fourier synthesis is that a phenyl group moves most in a direction roughly perpendicular to its plane. Another study of the vibrational behavior was made by doing a least-squares calculation on the temperature factors of the carbons only. The results were averaged and are given with respect to a B value of 3.20 common to all carbon atoms and with their average deviation in Table 9. Noteworthy is the fact that C(b) rather than C(c) has the largest temperature movement in all three phenyl groups. Theoretical values for ΔB can be calculated by assuming a torsional motion around the N-C bond and one, twice as large, around the C-C(e) bond. These are given in the second column of Table 9 and show close agreement with the experimental values ΔB . The qualitative influence on the bond lengths is that these motions should shorten the C(c)-C(d) bond the most. It does not explain the long C(d)-C(e) bond, however.

Table 9. Comparison of temperature factor corrections

	ΔB (exper.) average	ΔB (calc.) (see text)
C	0.00 ± 0.33	0
C(a)	$+1.64 \pm 0.24$	$+1.65$
C(b)	$+2.88 \pm 0.03$	$+2.75$
C(c)	$+2.09 \pm 0.14$	$+2.20$
C(d)	$+1.61 \pm 0.15$	$+1.65$
C(e)	$+0.55 \pm 0.23$	$+0.55$

Bryden (1959) has reported the structure of the dipotassium salt of methylenebisnitrosohydroxylamine. In Table 10 a comparison is made of the results of Bryden with those of the present investigation. There are three significant differences. The N(I)-O(I) bond in iron cupferron is considerably longer resulting in a greater negative charge on O(I), equaling the charge on O(II). This is probably due to the Fe^{3+} ion. The C-N(I) bond in iron cupferron is considerably shorter. Some shortening is caused by the sp^2 hybridization of C and N(I), while the bond might have a small amount of double bond character. The O(I)-O(II) distance in iron cupferron is considerably shorter. The double bond character in the N(I)-N(II) bond in iron cupferron is estimated at 50%, using Pauling's relation.

Table 10. Comparison of distances in the nitrosohydroxylamino groups

Methylenebis-nitrosohydroxylamine ion (Bryden, 1959)	Iron cupferron
N(I)-N(II)	1.297 Å
N(I)-O(I)	1.266
N(II)-O(II)	1.323
C-N(I)	1.512
O(I)-O(II)	2.566
	1.302 Å
	1.318
	1.314
	1.433
	2.447

The six measured Fe-O distances are quite closely the same with an average of 2.00 ± 0.01 Å (Lindqvist (1947), 2.08 Å in $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$, and Roof (1956), 1.95 Å in ferric acetylacetone). The octahedral surrounding of iron by the oxygen atoms is distorted to great extent in the structure of iron cupferron, as can be seen in Figs. 5 and 6, and Table 11, which lists all O-O distances in the octahedron. All bold-type and italic distances in Table 11 would be the same (2.83 Å) in a regular octahedron. The distortion can be described in two steps. The shape of the cupferron group and the effective radius of the Fe^{3+} ion limits the approach of the ligand and determines the O-Fe-O angle of 75° in the chelate group (italic distances in Table 11). The three pairs of oxygen atoms (O(1)O(4), O(2)O(5), and O(3)O(6)) could still maintain trigonal symmetry but do not. In essence chelate group DA (Fig. 6) is rotated downward (numbered molecule Fig. 5), resulting in van der Waals distances of O(1) with O(3) and O(5), and chelate group EB is rotated upward relative to group FC, giving close approaches of O(2) with O(4) and O(6).

Table 11. Oxygen distances in the octahedron (Å)

0	1	2	3	4	5
1					
2	3.33				
3	2.76	3.92			
4	2.45	2.81	3.15		
5	2.77	2.46	3.04	3.88	
6	3.92	2.72	2.43	3.02	3.19

The apparent ease and extent of the distortion indicates that the electronic structure of the Fe^{3+} ion in iron cupferron has spherical symmetry with each of the five $3d$ electrons occupying one of the five $3d$ orbitals, and that this configuration of the free ion is unchanged after the chelation. This deduction is qualitatively sustained by a measurement of magnetic susceptibility of the compound (Verkade & Piper, 1960). From these measurements the value 5.77 B.M. was calculated for the magnetic moment, considered by those workers to be significantly lower but close to the spin-only value 5.92 B.M. The conclusion of the present investigation, therefore, is that the Fe–O bonding in iron cupferron is, in crystal field terms, of the weak field type, which can be identified with ionic bonding.

Table 12. Shortest intermolecular distance of each type

N(3)–N(4)	(c)	3.51 Å
O(4)–O(5)	(c)	3.42
O(3)–N(4)	(c)	3.19
O(6)–C(3)	(d)	3.27
N(3)–C(10)	(a)	3.35
C(11)–C(13)	(a)	3.46

Table 13. Close contacts of each chelate group (Å)

Chelate group AD		Chelate group BE			
N(1)–C(18)	(c)	3.53	O(2)–C(14)	(c)	3.38
O(4)–C(9)	(a)	3.28	O(5)–N(4)	(c)	3.26
N(4)–O(3)	(c)	3.19	C(9)–O(4)	(a)	3.28
N(4)–O(5')	(c)	3.26	C(10)–N(3)	(a)	3.35
C(1)–C(18)	(c)	3.54	C(10)–N(6)	(a)	3.50
C(3)–O(6)	(d)	3.27	C(11)–C(13)	(a)	3.46
C(4)–O(6)	(d)	3.41	C(11)–C(14)	(a)	3.69

Chelate group CF					
O(3)–N(4)	(c)	3.19	C(13)–C(11)	(a)	3.46
O(6)–C(3)	(d)	3.27	C(13)–C(10)	(a)	3.56
O(6)–C(5)	(c)	3.36	C(14)–O(2)	(c)	3.38
O(6)–C(4)	(d)	3.41	C(14)–C(11)	(a)	3.69
N(3)–C(10)	(a)	3.35	C(16)–C(16)	(b)	3.66
N(6)–C(10)	(a)	3.50	C(18)–N(1)	(c)	3.53
			C(18)–C(1)	(c)	3.54

All possible intra- and intermolecular distances below 4.0 Å were calculated (van der Helm, 1960) as a final check on the structure. The smallest intermolecular distance of each type is given in Table 12, using the following code: The distances are given between an atom of the numbered molecule (Fig. 5) and an atom of a molecule related to the numbered molecule either by the screw axis (a), center of

symmetry (b), glide plane (c) or a translation in the c direction (d). It is clear that there are no abnormally short intermolecular distances.

The packing may be described in the following way (Table 13). The cupferron group *AD* had close contacts of atoms N(1), N(4) and C(1) with the molecule related by a glide plane (Figs. 5 and 6), and of C(3) and C(4) with the molecule translated in the c direction. The group *BE* has mainly close contacts with the molecule related by a screw axis (atoms C(9), C(10) and C(11)), and the third cupferron group *CF* has the most close contacts, which are approaches of atoms O(3), N(3), N(6), C(13) and C(14) with the molecule related by a screw axis, of atoms C(3), O(6), C(14) and C(18) with the molecule related by a glide plane and of atom O(6) with the molecule translated in the c direction, while there is C(16)–C(16) contact over the center of symmetry.

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