

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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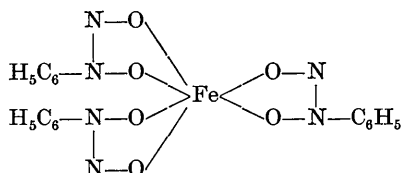
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The structure of iron cupferron, $\text{Fe}(\text{O}_2\text{N}_2\text{C}_6\text{H}_5)_3$, has been determined by three-dimensional Fourier and least-squares methods. The crystals are monoclinic with the unit-cell dimensions $a_0 = 12.50$, $b_0 = 17.45$, $c_0 = 11.15$ Å; $\beta = 122^\circ 19'$. 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 isomorphous 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 ($a = 5.639$ Å). Iron radiation was used throughout ($\lambda(K\alpha) = 1.936$ Å). 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_o for those reflections is half of the minimal structure factor amplitude which is observable at the position of the reflection

Table with multiple columns of h, k, l, F_o, F_c values for various reflections. The table is organized into several groups of columns, each representing different reflection indices. Values range from 0 to 1000, with some entries marked with asterisks to indicate unobserved reflections.

(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.

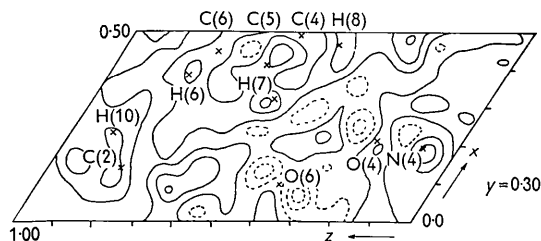


Fig. 1. Final difference Fourier synthesis at $y=0.30$. Contours are at intervals of $0.2 \text{ e.}\text{\AA}^{-3}$.

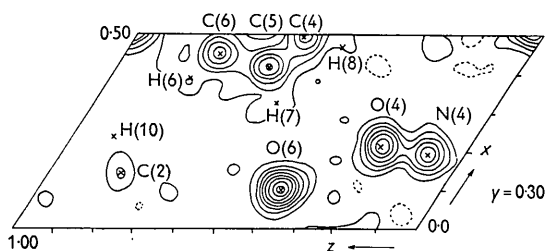


Fig. 2. Final Fourier synthesis at $y=0.30$. Contours are at intervals of $1.0 \text{ e.}\text{\AA}^{-3}$.

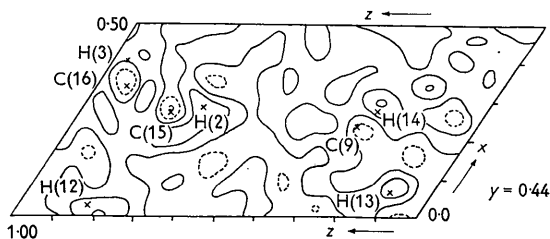


Fig. 3. Final difference Fourier synthesis at $y=0.44$. Contours are at intervals of $0.2 \text{ e.}\text{\AA}^{-3}$.

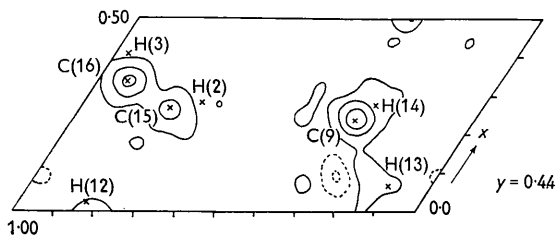


Fig. 4. Final Fourier synthesis at $y=0.44$. Contours are at intervals of $1.0 \text{ e.}\text{\AA}^{-3}$.

Table 2. Final coordinates and temperature factor coefficients

	x	y	z	B
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

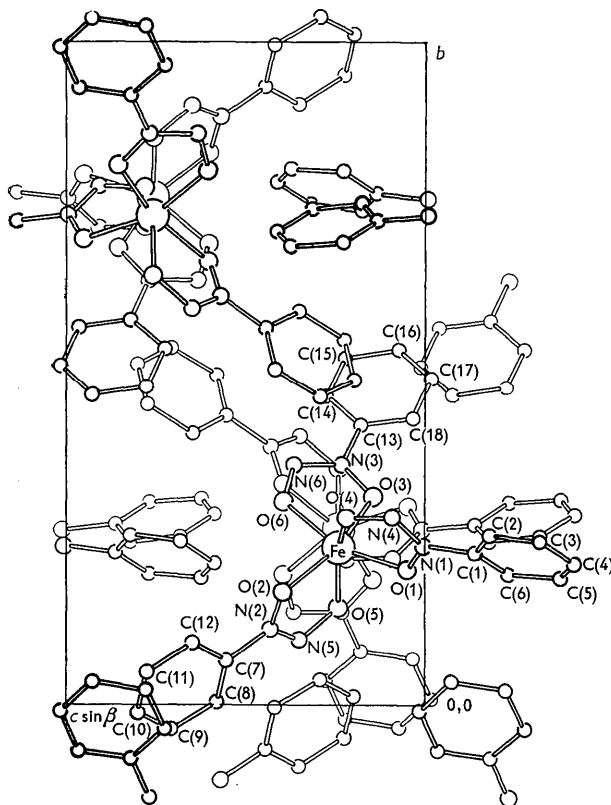
All computations were made on an IBM 650 electronic computer, equipped with magnetic tapes. The programs used in the present analysis, Fourier summation, structure-factor and least-squares calculations, were reported by two of us (Merritt & van der Helm, 1959). The scattering factors for carbon, nitrogen, 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	2.00 Å
Fe-O(4)	2.01	Fe-O(5)	2.01	Fe-O(6)	2.00	2.00
O(1)-N(1)	1.33	O(2)-N(2)	1.31	O(3)-N(3)	1.31	1.32
O(4)-N(4)	1.32	O(5)-N(5)	1.32	O(6)-N(6)	1.30	1.32
N(1)-N(4)	1.30	N(2)-N(5)	1.31	N(3)-N(6)	1.30	1.30
C(1)-N(1)	1.42	C(7)-N(2)	1.43	C(13)-N(3)	1.45	1.43
C(1)-C(2)	1.39	C(7)-C(8)	1.37	C(13)-C(14)	1.41	1.39
C(2)-C(3)	1.38	C(8)-C(9)	1.40	C(14)-C(15)	1.41	1.40
C(3)-C(4)	1.39	C(9)-C(10)	1.37	C(15)-C(16)	1.42	1.39
C(4)-C(5)	1.35	C(10)-C(11)	1.33	C(16)-C(17)	1.35	1.34
C(5)-C(6)	1.44	C(11)-C(12)	1.42	C(17)-C(18)	1.42	1.43
C(6)-C(1)	1.38	C(12)-C(7)	1.40	C(18)-C(13)	1.37	1.38

Table 4. Bond angles

				Average	
O(1)FeO(4)	75.6°	O(2)FeO(5)	75.6°	O(3)FeO(6)	75.5°
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				
	<i>R</i>	<i>S</i>	<i>T</i>	<i>d</i>	
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*
($\text{\AA} \times 10^{-3}$)

	<i>A</i>	<i>D</i>		<i>B</i>	<i>E</i>		<i>C</i>	<i>F</i>
C(1)	-5	-17	C(7)	-2	+10	C(13)	+1	+17
C(2)	+17	-242	C(8)	+2	-125	C(14)	+10	-231
C(3)	-6	-233	C(9)	-5	-30	C(15)	-15	-173
C(4)	-17	+32	C(10)	+8	+218	C(16)	+8	+189
C(5)	+28	+319	C(11)	-8	+337	C(17)	+3	+424
C(6)	-16	+250	C(12)	+4	+256	C(18)	-8	+336
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 \AA and 0.04 \AA . 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 $\begin{matrix} \text{N} \\ \diagup \\ \text{O} \end{matrix} \text{N-C}$ 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

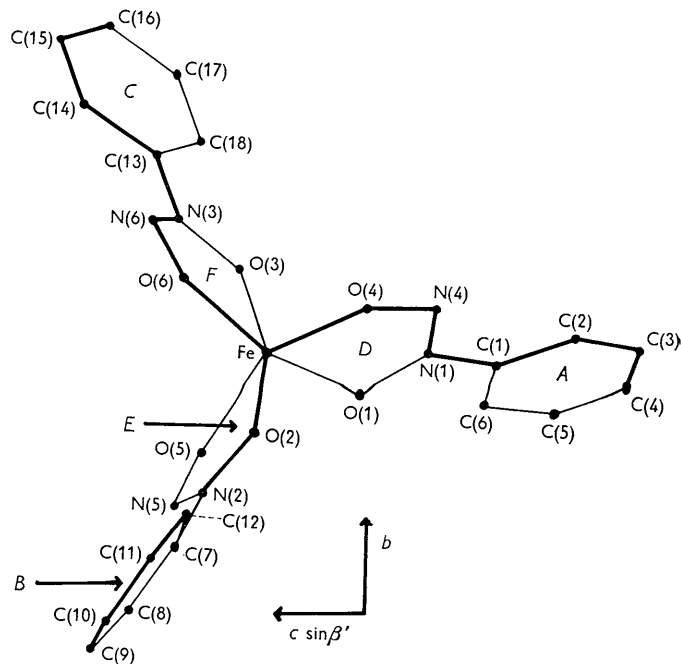


Fig. 6. A view of the molecule along the [101] direction.

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.

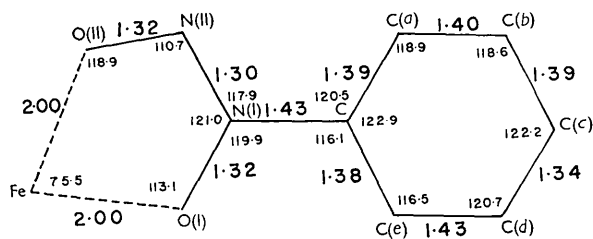


Fig. 7. The cupferron group. Bond distances and angles are average values from the three crystallographically independent cupferron groups (compare Tables 3 and 4).

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 \pm 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), equalling 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	1.302 Å
N(I)-O(I)	1.266	1.318
N(II)-O(II)	1.323	1.314
C-N(I)	1.512	1.433
O(I)-O(II)	2.566	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 $(NH_4)_2FeCl_5 \cdot H_2O$, and Roof (1956), 1.95 Å in ferric acetylacetonate). 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	<i>2.45</i>	2.81	3.15		
5	2.77	<i>2.46</i>	3.04	3.88	
6	3.92	2.72	<i>2.43</i>	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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