87. *The Crystal and Molecular Structure of Di[cyclohexane-1,2-dioximato(1-)]di-imidazoleiron(II) (Ferrous bisNioximebisimidazole).*

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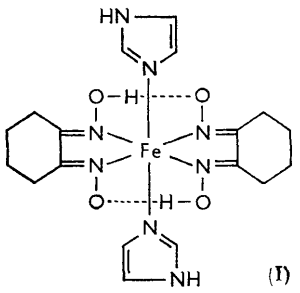
The crystal and molecular structure of the complex named in the title has been determined and refined by least-squares analysis on partial three-dimensional data. Factors affecting the orientation of the imidazole ring with respect to the planar dioxime system are discussed.

Complexes containing a central metal atom, a group of four ligands in a plane, as in porphyrin, and one or two other ligands completing an octehedron are of biological importance in the chlorophylls, the cobalamins, and the hæm compounds. Rather than investigating directly the properties of these complex molecules R. J. P. Williams and his co-workers [1] studied related series of molecules containing the same metal ion but simpler ligands. Such a molecule, a model of a hæm complex, di[cyclohexane-1,2-dioximato(1-)]di-imidazoleiron(II) (I) has been investigated to confirm the planarity of the dioxime system and to define the preferred orientation of the imidazole in the absence of a protein.



(I)

Crystal Data.—$H_{30}C_{18}FeN_8O_6$, $M = 423{\cdot}7$. Triclinic pinacoidal, $a = 9{\cdot}04 \pm 0{\cdot}03$, $b = 9{\cdot}02 \pm 0{\cdot}03$, $c = 9{\cdot}93 \pm 0{\cdot}03$ Å, $\alpha = 113{\cdot}4° \pm 0{\cdot}2°$, $\beta = 60{\cdot}1° \pm 0{\cdot}2°$, $\gamma = 120{\cdot}4° \pm 0{\cdot}2°$; $U = 671{\cdot}1$ Å^3. D_m(undetermined), $Z = 1$, $D_c = 1{\cdot}776$, $F(000) = 268$, $\mu = 70{\cdot}5$ cm.$^{-1}$. Space group, $P\bar{1}$ (C_i^1, No. 2); Cu-K_α radiation, single crystal oscillation and Weissenberg photographs. Optically biaxial.

A three-dimensional Patterson function sharpened to " point atoms at rest " was computed, from 863 independent reflections. The distribution could be interpreted on the assumption of the metal atom at a centre of symmetry. Minor peaks indicated preliminary light-atom positions. A complete set of atomic co-ordinates, including those of the water molecule O(3) not previously suspected from the analytical results, were obtained and were adjusted by using three-dimensional F_0 and difference syntheses phased on contributions from all atoms.

Nine cycles of least-squares refinement were evaluated, a block diagonal approximation to the normal matrix being used. The weighting function

$$\sqrt{\omega} = \sqrt{\frac{1}{1 + \left(\frac{|F_o| - b}{a}\right)^2}}$$

was used, a and b being given the values 1·5 and 3·5 on an absolute scale. Positions of hydrogen atoms were estimated, and anisotropic temperature factors were introduced after the third cycle. After the refinement the reliability index was 0·134.

Table 1 lists the observed and calculated structure factors based on the final atomic co-ordinates given in Table 2. The standard deviations are minimum values deduced from the

[1] Braterman, Davis, and Williams in " Structure and Properties of Biomolecules," Wiley, New York, in the press; Williams, in " Haematin Enzymes," eds. Falk, Lemberg, and Morton, Pergamon, London, 1961, p. 41; Cowan, Drake, and Williams, *Discuss. Faraday Soc.*, 1959, **27**, 217.

TABLE 1.

Observed structure amplitudes and calculated structure factors, rounded from the computer figures used in calculating R.

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
0	0	6	49	57			9	29	38			7	33	25			2	25	29
		5	96	94	1	−7	1	57	62			10	35	31			3	50	53
		4	75	69			2	50	46			11	31	35	1	7	−8	27	36
		3	31	33			3	72	64	1	1	−6	36	56			−5	21	14
		2	57	59			4	62	68			−5	30	44			−4	67	68
		1	194	241			5	69	75			−4	98	103			−3	98	92
0	1	−7	51	60			8	27	37			−3	205	234			−2	31	47
		−5	28	31			9	55	64			−2	73	−78			0	27	46
		−4	243	282	1	−6	0	85	87			−1	61	−57			1	45	52
		−3	221	251			1	124	95			0	62	51			2	54	41
		−2	382	402			2	52	49			1	475	516			3	24	56
		−1	44	29			3	26	34			2	205	191	1	8	−4	22	37
		0	231	231			4	46	58			3	25	−36			−3	30	47
		1	181	165			5	126	143			4	19	27			1	37	41
		2	114	−119			6	56	71			5	108	112	1	9	0	24	26
		3	142	122			9	23	28			6	51	45	2	−10	4	45	58
		4	32	53	1	−5	−1	87	87			7	98	90			5	28	42
		5	30	21			0	39	34			8	80	69			6	49	53
0	2	−7	60	49			1	131	119			9	32	33			7	44	50
		−6	89	89			2	109	105			10	29	47	2	−9	2	30	31
		−5	81	87			3	25	35			11	14	28			3	36	44
		−4	220	242			4	85	91	1	2	−6	34	46			4	70	71
		−3	102	114			5	94	99			−5	53	59			5	53	68
		−2	177	−172			6	77	82			−4	53	−49			6	36	50
		−1	44	−44			8	34	33			−3	203	201			7	34	40
		0	116	−107			9	48	50			−2	116	111	2	−8	1	80	95
		1	126	111			10	52	47			−1	20	19			2	79	67
		2	72	−44	1	−4	−2	38	−13			0	100	96			3	67	69
		3	81	79			−1	112	113			1	113	97			4	41	44
		4	52	51			0	76	31			2	74	79			5	30	26
		5	23	51			1	110	94			3	103	100	2	−7	0	67	87
0	3	−10	38	38			2	244	209			4	72	68			1	74	58
		−9	49	47			3	39	−11			5	109	103			2	62	50
		−8	70	65			5	43	51			6	89	84			3	31	30
		−7	60	63			6	40	44			7	65	62			8	28	16
		−6	55	63			7	80	85			8	90	82			10	43	45
		−5	21	19			8	96	97			10	43	25	2	−6	−2	35	62
		−3	47	−31			9	58	55	1	3	−8	24	34			−1	60	72
		−2	124	−109			10	36	32			−7	34	33			1	19	13
		−1	55	81			11	20	14			−5	52	64			2	21	−3
		0	39	−14	1	−3	−3	49	67			−4	46	52			3	26	24
		1	20	−3			−2	36	−18			−3	64	75			5	118	106
		3	64	56			−1	65	51			−2	101	90			6	103	114
		4	56	114			0	183	153			−1	74	62			7	33	−26
		5	34	94			1	27	11			0	59	57			8	31	32
0	4	−10	40	43			2	54	−45			1	125	119			9	50	50
		−9	48	52			4	57	64			2	37	39			10	104	90
		−8	70	76			5	187	216			3	80	72			11	35	32
		−7	30	25			6	85	87			4	117	120	2	−5	−2	29	50
		−4	76	62			8	44	44			5	50	50			−1	34	24
		−3	59	61			9	55	58			6	85	81			0	44	43
		−2	67	−39			10	44	37			7	31	12			1	106	77
		−1	95	85			11	44	44			10	19	27			3	113	105
		0	120	107	1	−2	−4	38	70	1	4	−9	36	49			4	51	57
		1	86	66			−3	95	87			−8	31	36			5	36	45
		2	169	157			−2	202	191			−7	47	61			6	217	224
0	5	−10	22	22			−1	105	−90			−6	34	45			7	107	109
		−9	23	13			0	57	−50			−4	62	67			8	61	53
		−8	39	40			1	172	179			−3	41	39			9	65	62
		−7	33	35			2	115	142			−2	46	46	2	−4	−2	113	−95
		−4	55	51			3	175	185			−1	63	63			−1	101	96
		−3	71	76			4	137	149			0	66	67			0	56	58
		−2	109	101			6	30	25			1	76	75			1	142	139
		−1	165	144			9	43	39			2	51	52			2	245	220
		0	184	175			10	22	21			3	18	15			3	156	141
		1	66	68			11	35	30			4	48	52			4	126	135
		4	28	−30	1	−1	−5	35	52			5	29	14			5	135	145
0	6	−10	12	15			−4	149	142			6	31	32			6	172	172
		−9	25	25			−3	44	33	1	5	−9	24	30			7	113	111
		−8	34	30			−2	152	156			−8	27	39			9	30	37
		−7	43	40			−1	88	91			−7	46	49	2	−3	−4	29	41
		−4	157	147			2	76	77			−6	27	48			−3	24	33
		−3	66	66			3	144	−162			−4	72	65			−2	49	−30
		−2	99	94			4	130	134			−3	94	94			−1	168	133
		−1	99	84			5	89	86			−2	28	30			0	207	175
		0	72	90			6	26	29			−1	41	40			1	81	77
		1	31	62			7	49	48			0	87	74			2	198	211
0	7	−7	43	48			8	27	16			1	52	55			3	217	204
		−6	22	32			11	22	26			2	56	60			4	89	93
		−4	124	114	1	0	−5	52	57	1	6	−8	14	26			5	43	46
		−3	52	41			−4	79	101			−7	29	40			9	70	73
		−2	21	25			−3	81	99			−6	40	44	2	−2	−4	131	149
0	8	−7	19	27			−2	146	178			−5	38	44			−3	167	135
		−6	24	21			−1	97	103			−4	69	63			−2	114	115
1	−9	4	28	36			2	75	−72			−3	60	61			−1	49	31
1	−8	2	36	53			3	17	−14			−2	34	33			0	133	123
		3	45	53			4	165	179			−1	48	57			2	155	180
		4	25	30			5	152	135			0	97	94			3	139	−137
		5	26	39			6	20	3			1	47	49			4	177	−152

TABLE 1. (*Continued.*)

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
		5	15	19			−3	65	68			7	100	93			8	63	57
		6	37	55			−2	27	36			8	54	43			9	70	62
		7	50	38			0	51	47	3	0	−4	41	65	4	−8	1	42	39
		8	29	20			1	55	55			−3	119	124			2	107	87
2	−1	−5	60	66	2	8	−3	32	46			−2	62	60			5	35	34
		−4	105	88			−2	58	56			−1	91	95			6	106	95
		−3	114	101			−1	22	30			0	82	72			7	77	74
		−2	145	161			0	27	37			1	68	−42			8	45	50
		−1	60	57			1	16	28			2	63	57			9	39	32
		3	28	26	3	−11	5	21	37			3	77	83	4	−7	−1	42	24
		4	60	−44	3	−10	3	24	8			4	53	55			1	70	−54
		5	135	130			5	63	68			5	109	106			2	89	83
		6	71	67			7	55	55			6	96	87			3	75	74
2	0	−5	107	108			8	36	38			7	34	39			4	74	78
		−4	68	72	3	−9	4	35	20	3	1	−4	61	65			5	86	77
		−3	51	49			5	88	89			−3	30	38			6	56	52
		−2	106	110			7	35	29			−2	38	48			8	52	59
		−1	42	45			8	44	39			0	70	75			9	38	30
		0	55	−56	3	−8	2	32	41			1	85	73	4	−6	−2	76	70
		2	39	47			3	54	52			2	264	256			0	52	35
		3	86	79			8	37	31			3	190	186			1	111	104
		4	45	37	3	−7	1	57	76			4	45	−10			2	108	98
		5	145	135			2	54	64			6	106	104			3	124	116
		6	175	163			3	34	11			7	31	64			4	66	61
		7	31	28			4	72	68	3	2	−4	38	54			5	39	31
		8	27	53			5	29	24			−2	117	110			6	40	50
2	1	−6	29	28			6	36	40			−1	114	113	4	−5	−3	31	22
		−5	75	81			7	32	16			0	99	86			−2	86	70
		−4	73	74			10	71	66			1	63	75			−1	140	140
		−3	67	80			11	41	40			2	122	108			0	100	86
		−2	49	41	3	−6	−1	34	63			3	183	160			1	213	208
		−1	139	142			0	22	94			4	68	61			2	75	78
		0	63	−49			1	29	40			5	29	35			4	29	37
		1	319	323			2	60	56			6	88	82			5	87	79
		2	327	333			4	111	104			7	32	42			6	30	37
		3	75	81			5	36	34	3	3	−4	67	65			7	129	116
		4	129	132			6	82	77			−3	40	36	4	−4	−3	136	132
		5	110	124			7	36	45			−2	96	80			−2	122	119
		6	95	109			8	30	39			−1	140	135			−1	89	79
2	2	−5	32	38			9	48	50			1	27	33			1	81	74
		−3	101	102			10	46	56			2	103	97			2	142	145
		−2	131	133			11	39	35			3	138	120			3	123	120
		−1	94	86	3	−5	−1	23	18			4	85	60			4	96	103
		0	55	52			0	87	103	3	4	−8	17	26			5	54	63
		1	149	160			1	129	130			−7	26	25			6	32	24
		2	347	345			2	158	141			−6	31	32			7	126	122
		3	73	71			3	55	41			−5	31	32			8	107	134
		4	23	28			4	37	28			−4	39	48	4	−3	−3	80	77
		5	33	52			5	84	80			−3	51	53			−2	68	72
		6	30	43			6	137	134			−1	93	89			−1	45	−44
2	3	−8	30	36			7	174	185			0	67	61			0	61	42
		−5	38	40			10	28	29			1	34	31			1	120	120
		−4	27	22			11	58	50			2	42	38			3	67	73
		−3	32	43	3	−4	0	167	173			4	32	6			4	154	165
		−2	175	151			1	86	75			5	46	44			5	85	86
		−1	100	103			2	57	51	3	5	−7	43	43			6	43	33
		0	84	80			3	241	247			−6	38	40			7	33	51
		1	32	−7			4	55	67			−5	46	43	4	−2	−4	41	−41
		2	51	51			5	97	104			−3	50	48			−3	77	62
		3	23	20			6	45	47			−2	46	48			−2	123	104
		4	22	30			7	123	124			−1	30	37			1	50	61
		5	28	72			8	68	61	3	6	−6	25	30			4	75	73
2	4	−8	28	35			10	48	29			−5	39	45			5	69	67
		−6	27	28			11	47	36			−2	36	25			6	79	73
		−5	32	40	3	−3	−3	26	83			1	42	43	4	−1	−6	33	32
		−4	55	60			−1	106	−102			2	54	48			−5	49	31
		−3	62	63			0	67	60			3	29	45			−3	57	38
		−2	89	84			1	156	168	3	7	−5	17	21			−2	106	102
		−1	31	−25			2	14	20			−4	23	15			−1	26	18
		0	29	−16			3	228	255			−3	45	17			1	46	52
		1	22	28			4	110	108			−2	45	49			3	70	75
		2	28	50			5	30	−16			−1	31	46			4	101	99
		3	40	48			6	92	93			0	42	37			5	38	58
2	5	−8	32	36			7	73	63			1	34	46			6	33	43
		−7	50	51			8	65	53	3	8	−2	29	47	4	0	−6	72	56
		−6	57	60			10	51	50			−1	16	42			−5	49	39
		−5	31	45			11	40	37	4	−11	2	30	49			−4	31	21
		−4	27	27	3	−2	−2	21	15			3	46	45			−2	67	67
		−2	33	39			−1	62	50			4	32	38			−1	97	105
		−1	26	26			0	54	47			5	38	42			0	61	57
		0	34	33			4	107	127			6	44	57			1	76	80
		1	87	83			5	45	−39	4	−10	1	36	60			2	79	81
2	6	−7	41	38			6	53	56			2	63	66			3	54	61
		−6	30	42			7	60	48			3	29	33			4	57	68
		−5	25	16			8	31	29			5	57	55			5	28	−24
		−4	29	32			9	46	42			6	40	34			6	29	7
		−3	62	59			10	72	72			7	32	34	4	1	−6	61	56
		−2	55	58	3	−1	−3	141	168	4	−9	1	48	63			−5	34	37
		−1	53	56			−2	110	102			2	73	62			−4	73	70
		1	57	62			−1	155	187			3	39	35			−3	79	81
		2	37	49			0	52	42			5	41	44			−2	51	51
2	7	−6	27	33			4	31	−15			6	58	52			−1	92	87
		−4	36	35			6	88	85			7	32	32			0	139	131

TABLE 1. (*Continued.*)

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
		1	54	67			7	73	79			8	132	107			3	46	57
		2	88	84			9	57	51			9	89	85			4	24	19
		3	52	60			10	79	63			11	32	32			5	39	32
		4	32	51	5	−7	3	107	127			12	44	44			6	41	37
4	2	−6	45	43			4	53	59	5	−3	4	85	97	5	1	−3	41	45
		−5	39	37			5	47	32			5	56	61			−2	83	73
		−4	42	49			6	34	26			6	52	69			−1	104	103
		−3	81	84			7	76	80			7	95	90			0	72	69
		−2	94	81			8	62	64			8	126	116			1	79	81
		−1	68	66			9	43	46			9	134	114			3	23	25
		0	78	82	5	−6	2	29	28	5	−2	−2	32	21			4	59	46
		2	63	63			3	123	116			−1	25	29	5	2	−3	80	77
4	3	−4	39	36			4	43	47			0	59	−54			−2	46	50
		−3	46	45			5	107	111			1	58	−47			−1	40	44
		−2	41	38			6	55	61			4	73	93			4	64	61
		−1	69	50			7	41	50			5	193	207	5	3	−3	37	26
		0	85	79	5	−5	1	85	97			6	246	88			−1	29	20
		1	78	62			2	112	89			9	44	57			0	48	42
		3	40	75			3	139	140	5	−1	−2	34	52			3	41	50
4	4	−3	46	23			4	61	54			−1	40	53			4	111	103
		−1	58	45			5	60	66			0	43	43			5	97	87
		0	48	37			6	38	49			2	89	102	5	4	0	61	60
4	6	0	51	44			8	48	41			3	139	166			1	56	62
4	7	−2	20	33			11	43	41			4	64	72			2	50	52
5	−11	7	39	48			12	62	55			5	95	98			3	38	50
5	−10	8	32	36	5	−4	−1	35	89			7	35	28			4	59	47
		9	24	28			0	41	82			8	67	58			5	46	52
5	−9	6	71	79			1	129	127			9	44	33	5	5	0	44	46
		7	48	57			2	134	142	5	0	−2	74	70			1	54	48
		8	46	50			3	64	68			−1	91	94			4	31	25
		9	31	56			4	37	36			0	102	101					
5	−8	4	43	52			5	53	−37			1	121	123					
		6	76	81			6	50	47			2	44	57					

TABLE 2.

Atomic co-ordinates (× 10^4) and standard deviations (× 10^4).

	x/a	$\sigma(x)$	y/b	$\sigma(y)$	Z/c	$\sigma(z)$		x/a	$\sigma(x)$	y/b	$\sigma(y)$	Z/c	$\sigma(z)$
Fe	0	0	0	0	0	0	C(9)	1841	31	3419	25	1647	21
N(1)	2076	20	1984	16	735	16	H(1)	2500		−1160		−2000	
N(2)	707	20	−1574	17	253	16	H(2)	5000		−1160		3500	
N(3)	−1601	21	−293	16	2136	15	H(3)	3430		1500		4830	
O(1)	2087	19	−2147	15	−870	15	H(4)	−3000		−1000		5000	
O(2)	−2891	19	483	15	2993	13	H(5)	−3500		2830		4000	
O(3)	3577	19	−2124	16	3798	15	H(6)	−2660		−3000		5660	
C(1)	−104	26	−2037	23	1648	19	H(7)	−1500		−670		5320	
C(2)	−1567	26	−1294	23	2731	20	H(8)	−2500		−4330		3660	
C(3)	−2655	34	−1773	26	4339	23	H(9)	−1330		−4660		4000	
C(4)	−1784	47	−2436	38	4884	27	H(10)	170		−4330		1000	
C(5)	−1129	40	−3746	28	3661	24	H(11)	1330		−2660		2330	
C(6)	236	34	−3171	25	2122	23	H(12)	4430		1660		0	
C(7)	3845	27	2230	26	552	26	H(13)	5820		3830		1500	
C(8)	4750	28	3832	27	1293	24	H(14)	3000		5000		2760	
N(4)	3472	24	4585	22	2006	19	H(15)	1000		3330		2000	

TABLE 3.

Thermal parameters (× 10^4). The temperature factor, T, is equal to $2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)}$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}		b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Fe	143	72	103	52	−110	86	C(3) ...	555	274	143	135	−27	372
N(1) ...	210	181	126	1	−192	298	C(4) ...	1053	711	161	299	237	1553
N(2) ...	199	188	116	8	−59	219	C(5) ...	884	351	166	187	138	959
N(3) ...	321	156	103	18	−4	374	C(6) ...	601	262	178	147	−294	339
O(1) ...	370	220	225	187	27	351	C(7) ...	93	356	404	372	−307	43
O(2) ...	378	226	118	57	−49	338	C(8) ...	209	333	246	111	−163	211
O(3) ...	325	234	193	−17	−138	228	N(4) ...	321	381	230	277	−267	107
C(1) ...	357	273	98	64	17	465	C(9) ...	390	362	145	108	19	684
C(2) ...	230	289	124	107	−56	302							

block diagonal approximation to the normal matrix. The thermal parameters are given in Table 3. The atomic co-ordinates in Table 4 are referred to a set of orthogonal axes X', Y', and Z' with their origin at the cell origin and defining the least-squares best plane through the metal atom and the dioxime ring systems (Fig. 1). The transformation matrix from the

orthogonal co-ordinates (in Å) referred to *a*, *b'*, and c*, (*b'* is on the same side of the *ac** plane as the crystallographic *b*-axis) to these co-ordinates is:

$$\begin{pmatrix} -0.4777 & 0.6378 & -0.6042 \\ 0.6676 & -0.1836 & -0.7215 \\ 0.5711 & 0.7480 & 0.3381 \end{pmatrix}$$

Interatomic distances and angles, together with standard deviations deduced from the formulæ of Cruickshank and Ahmed [2] and Darlow,[3] are listed in Table 5.

Results.—The crystal is composed of centrosymmetric neutral complex molecules and water molecules. The water molecules are not attached to the metal atoms but connect the complexes by a network of hydrogen bonds.

In the complex, the iron atom is at the centre of a distorted octahedron of six nitrogen atoms, four from two dioxime molecules and at an average distance of 1·94 Å, and two

TABLE 4.

Atomic co-ordinates (Å) referred to a set of orthogonal axes defining the least-squares best plane through the iron atom and the dioxime ring system.

	X'	*Y'*	*Z'*		*X'*	*Y'*	*Z'*
Fe	0	0	0	C(3)	−3·8240	−1·8844	−0·0195
N(1)	−0·1071	0·1828	2·0343	C(4)	−5·1380	−1·1976	0·4584
N(2)	−1·6453	1·0679	−0·0286	C(5)	−5·3127	0·0874	−0·1655
N(3)	−1·3410	−1·3646	0·0253	C(6)	−4·1778	1·0351	0·0426
O(1)	−1·6922	2·4361	0·0027	C(7)	−0·5295	1·1735	2·9353
O(2)	−0·9615	−2·7031	−0·0110	C(8)	−0·4179	0·8313	4·2559
O(3)	−6·3036	2·1672	2·8491	N(4)	0·0631	−0·4537	4·1534
C(1)	−2·8169	0·4404	0·0216	C(9)	0·2405	−0·8273	2·7779
C(2)	−2·5780	−1·0438	−0·0158				

TABLE 5.

Some interatomic distances (Å) and angles. (Numbers in parentheses are standard deviations.)

Fe–N(1)	2·05	(0·02)	C(7)–C(8)	1·38	(0·04)	O(2)–N(3)–C(2)...	120·3	(2·2)
Fe–N(2)	1·97	(0·01)	C(8)–N(4)	1·37	(0·03)	N(2)–C(1)–C(2)...	109·5	(1·5)
Fe–N(3)	1·91	(0·02)	N(4)–C(9)	1·45	(0·04)	N(2)–C(1)–C(6)...	127·6	(2·4)
N(1)–C(7)	1·40	(0·03)	N(1)–Fe–N(2) ...	85·5	(0·7)	C(2)–C(1)–C(6) ...	122·9	(2·3)
N(1)–C(9)	1·30	(0·03)	N(1)–Fe–N(3) ...	90·8	(0·9)	N(3)–C(2)–C(3)...	131·3	(1·4)
N(2)–O(1)	1·35	(0·03)	N(2)–Fe–N(3) ...	78·8	(0·8)	C(1)–C(2)–C(3) ...	115·0	(1·6)
N(2)–C(1)	1·34	(0·03)	Fe–N(1)–C(7) ...	135·4	(1·7)	C(2)–C(3)–C(4) ...	117·0	(3·0)
N(3)–O(2)	1·39	(0·03)	Fe–N(1)–C(9) ...	118·7	(1·9)	C(3)–C(4)–C(5) ...	111·5	(2·3)
N(3)–C(2)	1·28	(0·02)	C(7)–N(1)–C(9)...	105·9	(2·3)	C(4)–C(5)–C(6) ...	114·5	(2·7)
C(1)–C(2)	1·50	(0·04)	Fe–N(2)–O(1) ...	125·1	(1·3)	C(1)–C(6)–C(5) ...	116·0	(2·6)
C(1)–C(6)	1·49	(0·02)	Fe–N(2)–C(1) ...	118·0	(1·5)	N(1)–C(7)–C(8)...	114·4	(2·3)
C(2)–C(3)	1·50	(0·04)	O(1)–N(2)–C(1)	116·7	(1·4)	C(7)–C(8)–N(4)...	101·0	(2·4)
C(3)–C(4)	1·56	(0·03)	Fe–N(3)–O(2) ...	119·7	(1·0)	C(8)–N(4)–C(9)...	111·3	(2·3)
C(4)–C(5)	1·44	(0·05)	Fe–N(3)–C(2) ...	119·9	(1·8)	N(1)–C(9)–N(4)	107·5	(2·3)
C(5)–C(6)	1·49	(0·05)						

from the two imidazole groups at a distance of 2·05 Å. The angle N(2)–Fe–N(3) is 78·8°, being approximately the same as is observed in the copper [4] and the nickel [5] dimethylglyoxime complex. The bond to imidazole makes an angle of 4·5° to the normal to the plane of the complex. This is probably a steric effect of the hydrogen bonding.

The structure of the chelate rings resembles very closely those observed in dimethylglyoxime complexes, with the carbon–nitrogen bonds apparently localized and the carbon–carbon bond single. The hydrogen bond O(1)–O(2)' (2·67 Å) is closer to the average O–H • • • O bond length than to the exceptionally short bonds (2·44 and 2·53 Å) observed for dimethylglyoxime complexes.

[2] Cruickshank and Ahmed, *Acta Cryst.*, 1953, **6**, 385.
[3] Darlow, *Acta Cryst.*, 1960, **13**, 683.
[4] Godycki and Rundle, *Acta Cryst.*, 1953, **6**, 487.
[5] Frasson, Bordi, and Bezzi, *Acta Cryst.*, 1959, **12**, 201.

The cyclohexane ring has the form observed by Ottar [6] for 1,2-epoxycyclohexane. The atoms C(4) and C(5), lying, respectively, above and below the planar system have large thermal vibration parameters and are believed to be either executing very large thermal vibrations or disordered so that in a certain proportion of the molecules they occupy positions analogous to those observed but with the Z' co-ordinates (Fig. 1) interchanged and changed in sign. Unsuccessful attempts were made to determine the occupation numbers for postulated disordered structures.

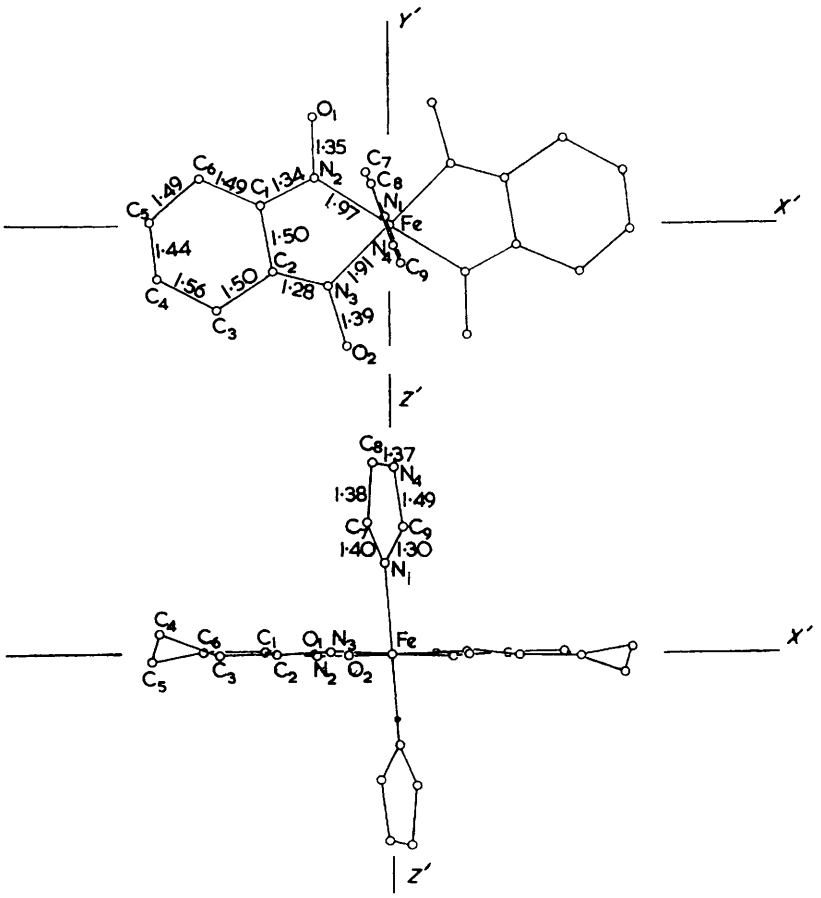


FIG. 1. The molecule (I) projected on to the best plane through the iron atom and the atoms of the chelate rings and a projection perpendicular to this plane. Some interatomic distances are given (in Å).

The imidazole group is planar and exhibits an alternation of double and single bonds as predicted by Williams's postulate of an uncharged species. The plane of the imidazole makes an angle of 11° to a plane bisecting the N(2)–Fe–N(3′) angle and normal to the dioxime plane. The orientation of the ring appears to be independent of the *d*-electron system of the iron atom and to depend mainly on the hydrogen-bond system and to a smaller extent on packing with respect to imidazole rings of other molecules. There is a tendency in this molecule, and in vitamin B_{12} [7] and its derivatives, for the ring system to avoid a plane containing the nitrogen atoms of the other ligands.

[6] Ottar, *Acta Chem. Scand.*, 1947, **1**, 283.
[7] Hodgkin, Kamper, Lindsey, Mackay, Pickworth, Robertson, Shoemaker, White, Prosen, and Trueblood, *Proc. Roy. Soc.*, *A*, **242**, 251.

Each water molecule is involved in the formation of three hydrogen bonds, two to two oxygen atoms, O(2) and O(2'), forming an approximately square-planar network linking O(2), O(3), O(2'), and O(3') (Fig. 2), and one to the nitrogen atom, N(4), *i.e.*, to the imidazole-nitrogen atom not attached to the metal. The neutral complexes are bound together in sheets parallel to the crystal plane (121) by hydrogen bonding, the sheets being held together by van der Waal's forces.

Experimental.—Preparation. The compound was prepared by a method devised by Davies and Williams.[8] 0·1N-Ferrous sulphate (1·8 ml.) in 0·1N-sulphuric acid (20 ml.) was added to a mixture of N/25-solution (18 ml.) of the dioxime, a 0·2N-solution (57 ml.) of imidazole, and water (75 ml.) with complete exclusion of oxygen. The mixture was kept for 30 hr. under

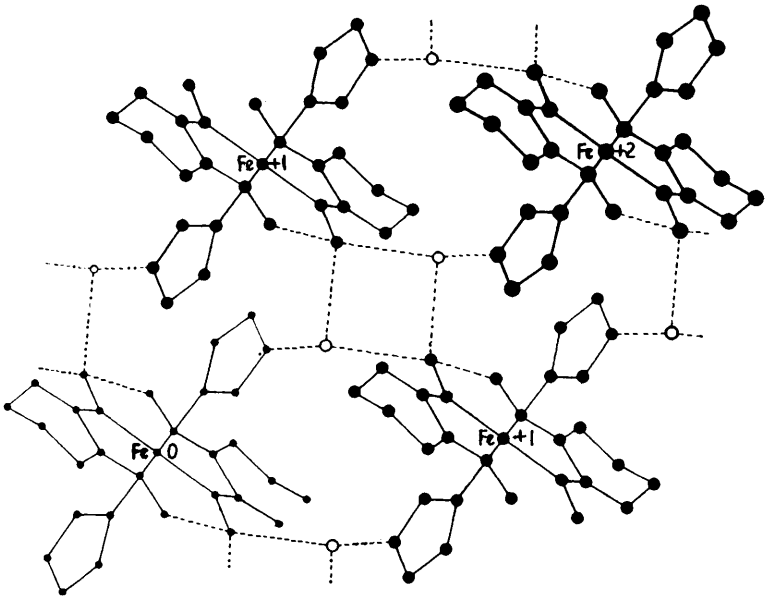


FIG. 2. The molecule (I) projected perpendicular to the (010) plane of the crystal, showing the environment of the water molecule O(3) and the hydrogen-bond system. The relative heights of the iron atoms at the centre of each molecule are indicated.

pure nitrogen. Deep magenta crystals (40 mg.) were formed. They were filtered off, washed rapidly with water, then with 1 : 1 v/v water–ethanol, and were stored under nitrogen in a vacuum-desiccator.

X-*Ray photography.* The crystals were sealed in Lindemann glass capillary tubes. The unit-cell dimensions were obtained from zero-layer Weissenberg photographs about the *a*-, *b*-, and *c*-axis, calibrated by means of the diffraction pattern of a copper wire. *X*-Ray intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs about the *a*-axis, obtained from a small plate crystal presenting a maximum thickness of 0·03 mm. to the *X*-ray beam. Similar intensities from photographs about the *b*-axis were used to obtain an approximate common scale for the observations (method of Rollett and Sparks [9]). The crystals had suffered from oxidation by this stage, and the *b*-axis data were not further used in the structure determination. The intensities were corrected for Lorentz and polarization factors, but not for absorption and extinction effects.

Calculations. These were carried out on a Ferranti "Mercury" computer. Structure factors and cycles of least-square refinement were calculated by using Rollett's "SFLS"

[8] Davies and Williams, personal communication.
[9] Rollett and Sparks, *Acta Cryst.*, 1960, **13**, 273.

programme.[10] Atomic scattering factors for nitrogen, carbon, and oxygen were as given by Berghuis *et al.*,[11] for hydrogen by McWeeny,[12] and for iron by Thomas and Umeda.[13] For Fourier syntheses Mills's general Fourier synthesis programme [10] was used, and for interatomic distances and angles Sparks's programme.[10]

We thank Professor D. C. Hodgkin, F.R.S., for her interest, the Director and Staff of the Oxford University Computing Laboratory (in particular, Dr. J. S. Rollett) for computing facilities, and the Pressed Steel Company for a research fellowship to C. K. P.

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[10] Mills and Rollett in " Computing Methods and the Phase Problem in *X*-ray Crystal Analysis," Pergamon, London, 1961, p. 107.
[11] Berghuis, Haanapel, Potters, Loopstra, MacGillavry, and Veenendal, *Acta Cryst.*, 1955, **8**, 478.
[12] McWeeny, *Acta Cryst.*, 1951, **4**, 513.
[13] Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.