Metal–Carbonyl and Metal–Nitrosyl Complexes. Part XV.[1] Crystal and Molecular Structure of (3-Formyl-*N*-ethoxycarbonylazepine)tricarbonyl-iron(0) †

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The molecular geometry of the title compound has been determined by single-crystal X-ray analysis from diffracto-meter data; the positional and thermal parameters of the atoms were obtained by Fourier and least-squares pro-cedures and the final value of R was 4·6% over 2363 independent reflections. The tricarbonyliron group binds to the C(4), C(5), C(6), C(7)-butadiene fragment of the azepine ring, with Fe–C(4), C(7) distances of 2·151 and 2·096(4) Å and Fe–C(5), C(6) distances of 2·053 and 2·051(4) Å. The bond lengths in the azepine ring are: N(1)–C(2) 1·379, C(2)–C(3) 1·347, C(3)–C(4) 1·465, C(4)–C(5) 1·431, C(5)–C(6) 1·406, C(6)–C(7) 1·431, and C(7)–N(1) 1·447 Å, all with σ *ca.* 0·005 Å. The ring has two nearly planar groups of atoms, (i) C(4), C(5), C(6), C(7), and (ii) C(7), N(1), C(2), C(3), C(4), the dihedral angle between the planes being 138°. The crystals are triclinic, space group $P\bar{1}$, with a = 7·022(3), b = 10·550(4), c = 9·500(3) Å, α = 92° 49(2)′, β = 94° 32(2)′, γ = 96° 8(2)′, and Z = 2.

DISCUSSION of the nature of the stable bond formed between the iron atom and olefins has been aided by X-ray diffraction studies of a wide range of dienetri-

carbonyliron complexes.[2-4] The results reveal that the iron atom is bound to a planar *cis*-butadiene C_4-fragment, with a substantial alteration in the molecular geometry of the olefinic ligand: thus, *e.g.*, the characteristic ' tub '

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conformation of cyclo-octatetraene (cot) is greatly altered on formation of $(cot)Fe(CO)_3$ and $(cot)[Fe(CO)_3]_2$,[5] geometrical isomerization occurs when vitamin-A aldehyde forms a tricarbonyliron complex,[6] and in all the complexed dienes the two outer carbon–carbon bonds are notably longer and the central carbon–carbon bond is notably shorter than in uncomplexed butadiene. The

(1)   (2)
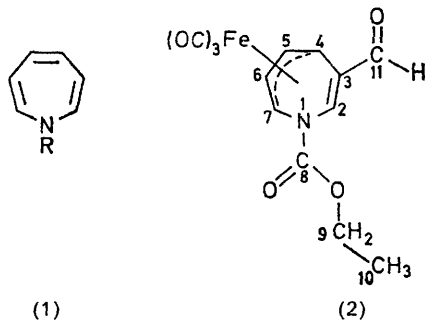
heterocyclic azepine ring (1) in N-p-bromobenzenesulphonylazepine [7] and N-phenoxycarbonylazepine [8] exists in a boat conformation with localized double bonds, whereas in the complexes (1H-azepine)tricarbonyliron,[9] (N-methoxycarbonylazepine)tricarbonyliron,[10] and (3-acetyl-1H-azepine)tricarbonyliron,[11] where the tricarbonyliron group is bound to the C(4), C(5), C(6), C(7)-butadiene moiety, the ring is divided into two almost planar sets of atoms hinged about the C(4) $\cdots$ C(7) line and inclined at a dihedral angle of $ca.$ 140°. Since the unsubstituted, 1-substituted, and 3-substituted complexes show interesting small variations in molecular geometries, we undertook an X-ray analysis of a 1,3-disubstituted complex, (3-formyl-N-ethoxycarbonylazepine)tricarbonyliron (2),[12] in order to extend our knowledge of the bonding in azepinetricarbonyliron complexes.

X-Ray intensity data for (2) were measured on a Hilger and Watts Y290 diffractometer and the positional and thermal parameters of the atoms determined by Fourier and least-squares procedures, the final value of R being 4·6% over 2363 reflections. The molecular structure is shown in Figure 1 and the arrangement of molecules in the unit cell in Figure 2. The atomic co-ordinates are listed in Table 1 and the bond lengths are compared with those of related complexes in Table 2. Other interatomic distances and angles are given in Tables 3 and 4, and the displacements of the atoms from various planes are in Table 5.

The X-ray analysis confirms that the tricarbonyliron group is bound to the C(4), C(5), C(6), C(7)- rather than the C(2), C(3), C(4), C(5)-butadiene fragment of the azepine ring. The iron atom is significantly closer to the central than to the terminal atoms of the butadiene; the

respective mean Fe–C distances are 2·05 and 2·12 Å, in good agreement with values in other dienetricarbonyliron complexes, $cf.$ 2·05 and 2·13 Å in (sorbic acid)tricarbonyliron.[13] The Fe–C(4) and Fe–C(7) distances actually show a significant asymmetry (2·151 and 2·096 Å) which is also a feature of (N-methoxycarbonylazepine)tricarbonyliron [10] but is much less evident in the 1H-azepine complexes.[9,11] The outer (1·431 Å) and central (1·406 Å) carbon–carbon bonds of the complexed C_4-fragment are appreciably different from those in uncomplexed butadiene (1·344 and 1·467 Å),[14] consistent with appreciable back donation of electrons from the
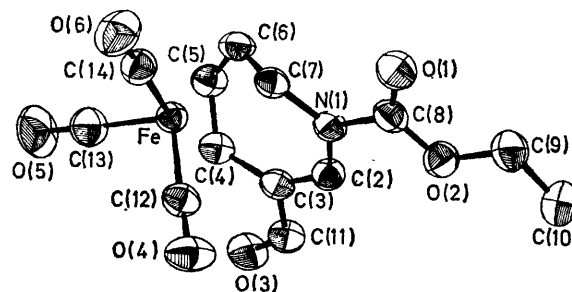

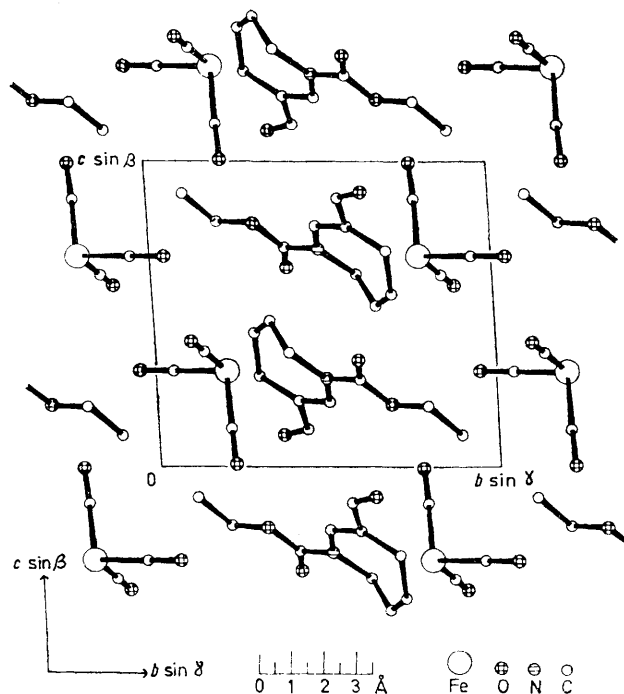FIGURE 1   The molecular structure of (3-formyl-N-ethoxycarbonylazepine)tricarbonyliron

FIGURE 2   The crystal structure of (3-formyl-N-ethoxycarbonylazepine)tricarbonyliron, viewed along the a axis

metal atom into the lowest antibonding molecular orbital of the butadiene.

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Uncomplexed azepine derivatives exhibit a boat conformation with C(2), C(3), C(6), and C(7) effectively coplanar.[7,8] In the complex (2) the ring has two nearly planar groups of atoms (i) C(4), C(5), C(6), C(7), and (ii) C(7), N(1), C(2), C(3), C(4) inclined at a dihedral angle of 138°, and this conformation is common to the other azepinetricarbonyliron complexes. Another striking

TABLE 1

Atomic co-ordinates, as fractions of the cell edges, with standard deviations in parentheses

	x	y	z
Fe	0·09012(7)	0·20994(4)	0·31160(5)
N(1)	0·1772(4)	0·5013(3)	0·2865(3)
C(2)	0·0021(5)	0·5073(3)	0·2120(4)
C(3)	−0·1513(5)	0·4191(4)	0·2140(4)
C(4)	−0·1667(5)	0·3045(4)	0·2952(4)
C(5)	−0·0889(6)	0·2960(4)	0·4377(4)
C(6)	0·1035(6)	0·3445(4)	0·4764(4)
C(7)	0·2191(5)	0·3954(3)	0·3705(4)
C(8)	0·3282(5)	0·5996(3)	0·2831(4)
C(9)	0·4255(7)	0·7983(4)	0·1970(5)
C(10)	0·3369(9)	0·8929(5)	0·1066(6)
C(11)	−0·3188(5)	0·4402(4)	0·1210(4)
C(12)	0·1243(5)	0·2170(4)	0·1257(4)
C(13)	−0·0495(6)	0·0558(4)	0·3116(5)
C(14)	0·3105(6)	0·1500(4)	0·3728(4)
O(1)	0·4821(4)	0·5994(3)	0·3480(3)
O(2)	0·2767(4)	0·6911(3)	0·2021(3)
O(3)	−0·4677(4)	0·3699(3)	0·1045(4)
O(4)	0·1398(5)	0·2252(4)	0·0095(3)
O(5)	−0·1322(6)	−0·0425(4)	0·3124(5)
O(6)	0·4497(5)	0·1128(3)	0·4102(4)
H(2)	−0·010(5)	0·582(3)	0·162(4)
H(4)	−0·290(5)	0·256(3)	0·274(3)
H(5)	−0·157(7)	0·239(4)	0·495(5)
H(6)	0·159(6)	0·340(4)	0·567(4)
H(7)	0·349(5)	0·406(3)	0·404(4)
H(9a)	0·548(8)	0·763(5)	0·150(6)
H(9b)	0·445(7)	0·837(5)	0·283(5)
H(10a)	0·312(10)	0·861(6)	0·018(7)
H(10b)	0·407(8)	0·965(6)	0·105(5)
H(10c)	0·214(10)	0·914(7)	0·157(7)
H(11)	−0·307(6)	0·528(4)	0·076(4)

TABLE 2

Bond lengths (Å) in (A) (3-formyl-N-ethoxycarbonylazepine)tricarbonyliron, (B) (N-methoxycarbonylazepine)tricarbonyliron, (C) (3-acetyl-1H-azepine)tricarbonyliron, and (D) (1H-azepine)tricarbonyliron; bonds numbered as in (2)

Bond	(A)	(B)	(C)	(D)
N(1)−C(2)	1·379(4)	1·382(11)	1·343(8)	1·352(7)
N(1)−C(7)	1·447(5)	1·436(11)	1·391(10)	1·402(6)
C(2)−C(3)	1·343(5)	1·334(14)	1·364(12)	1·322(7)
C(3)−C(4)	1·465(5)	1·439(14)	1·458(11)	1·451(7)
C(4)−C(5)	1·431(5)	1·398(14)	1·457(10)	1·414(7)
C(5)−C(6)	1·406(6)	1·409(13)	1·392(13)	1·407(7)
C(6)−C(7)	1·431(5)	1·440(12)	1·464(13)	1·409(7)
C(3)−C(11)	1·458(5)		1·467(9)	
N(1)−C(8)	1·406(5)	1·372(11)		
C(8)−O(1)	1·201(5)	1·192(12)		
C(8)−O(2)	1·325(5)	1·334(12)		
O(2)−C(9)	1·461(5)	1·465(15)		
C(9)−C(10)	1·507(7)			
Fe−C(4)	2·151(4)	2·145(10)	2·182(7)	2·206(5)
Fe−C(5)	2·053(4)	2·059(10)	2·063(8)	2·033(5)
Fe−C(6)	2·051(4)	2·041(9)	2·055(9)	2·039(5)
Fe−C(7)	2·096(4)	2·091(8)	2·168(9)	2·174(4)
Fe−C(12)	1·805(4)	1·713(11)	1·791(8)	1·765(4)
Fe−C(13)	1·807(4)	1·784(10)	1·799(10)	1·779(4)
Fe−C(14)	1·799(4)	1·779(10)	1·802(6)	1·782(4)
C(12)−O(4)	1·125(5)	1·153(14)	1·138(10)	1·142(6)
C(13)−O(5)	1·134(6)	1·123(12)	1·148(14)	1·138(5)
C(14)−O(6)	1·136(5)	1·142(13)	1·137(9)	1·144(6)

TABLE 3

Valency angles (°)

C(12)−Fe−C(13)	100·3(2)	N(1)−C(8)−O(2)	113·3(3)
C(12)−Fe−C(14)	99·8(2)	O(1)−C(8)−O(2)	125·5(3)
C(13)−Fe−C(14)	93·4(2)	C(8)−O(2)−C(9)	114·2(3)
Fe−C(12)−O(4)	176·9(4)	O(2)−C(9)−C(10)	106·0(4)
Fe−C(13)−O(5)	178·0(4)	C(3)−C(11)−O(3)	125·2(4)
Fe−C(14)−O(6)	179·3(4)	C(3)−C(11)−H(11)	114(2)
Fe−C(4)−C(5)	66·5(2)	O(3)−C(11)−H(11)	121(2)
Fe−C(4)−C(3)	114·2(2)	N(1)−C(2)−H(2)	116(2)
Fe−C(7)−C(6)	68·1(2)	C(3)−C(2)−H(2)	119(2)
Fe−C(7)−N(1)	120·6(2)	C(3)−C(4)−H(4)	110(2)
C(4)−Fe−C(5)	39·7(1)	C(5)−C(4)−H(4)	114(2)
C(4)−Fe−C(6)	71·2(2)	C(4)−C(5)−H(5)	118(3)
C(4)−Fe−C(7)	82·5(1)	C(6)−C(5)−H(5)	121(3)
C(5)−Fe−C(6)	40·1(2)	C(5)−C(6)−H(6)	122(2)
C(5)−Fe−C(7)	72·3(1)	C(7)−C(6)−H(6)	119(3)
C(6)−Fe−C(7)	40·4(1)	C(6)−C(7)−H(7)	110(2)
N(1)−C(2)−C(3)	124·3(3)	N(1)−C(7)−H(7)	109(2)
C(2)−C(3)−C(4)	127·8(3)	O(2)−C(9)−H(9a)	108(3)
C(2)−C(3)−C(11)	115·2(3)	O(2)−C(9)−H(9b)	107(3)
C(4)−C(3)−C(11)	117·0(3)	H(9a)−C(9)−H(9b)	118(4)
C(3)−C(4)−C(5)	125·8(3)	C(10)−C(9)−H(9a)	111(3)
C(4)−C(5)−C(6)	119·1(3)	C(10)−C(9)−H(9b)	105(3)
C(5)−C(6)−C(7)	119·1(3)	C(9)−C(10)−H(10a)	111(4)
C(6)−C(7)−N(1)	125·0(3)	C(9)−C(10)−H(10b)	114(4)
C(7)−N(1)−C(2)	123·2(3)	C(9)−C(10)−H(10c)	104(4)
C(7)−N(1)−C(8)	115·9(3)	H(10a)−C(10)−H(10b)	109(6)
C(8)−N(1)−C(2)	120·9(3)	H(10a)−C(10)−H(10c)	114(6)
N(1)−C(8)−O(1)	123·1(3)	H(10b)−C(10)−H(10c)	105(5)

TABLE 4

Intermolecular separations (Å)

O(3) · · · O(4I)	3·05	O(3) · · · C(9V)	3·34
O(6) · · · O(6II)	3·11	O(2) · · · O(3V)	3·36
O(3) · · · C(12I)	3·16	O(2) · · · C(11V)	3·36
O(1) · · · C(11III)	3·17	O(3) · · · C(11VI)	3·38
O(1) · · · C(6IV)	3·22	O(3) · · · C(8I)	3·39
O(1) · · · C(7IV)	3·26	O(5) · · · C(9VII)	3·44
O(1) · · · O(3III)	3·33	N(1) · · · C(5VIII)	3·44

The superscripts refer to the following transformations of the atomic co-ordinates:

I	−1 + x, y, z	V	−x, 1 − y, −z
II	1 − x, −y, 1 − z	VI	−1 − x, 1 − y, −z
III	1 + x, y, z	VII	−1 + x, −1 + y, z
IV	1 − x, 1 − y, 1 − z	VIII	−x, 1 − y, 1 − z

TABLE 5

Displacements (Å) of the atoms from various planes; atoms not included in the derivation of a plane are italicized

Plane (a): C(4) −0·007, C(5) 0·014, C(6) −0·014, C(7) 0·007, H(4) 0·17, H(5) 0·28, H(6) 0·00, H(7) 0·19, Fe 1·588

Plane (b): C(7) 0·023, N(1) −0·029, C(2) 0·004, C(3) 0·022, C(4) −0·021, C(8) −0·097, C(11) 0·135

Plane (c): C(3) 0, C(4) 0, C(5) 0, H(4) −0·54

Plane (d): C(6) 0, C(7) 0, N(1) 0, H(7) −0·63

Plane (e): C(7) 0, C(8) 0, C(2) 0, N(1) −0·006

Plane (f): C(8) −0·007, O(1) −0·007, O(2) 0·011, C(9) 0·019, C(10) −0·017, N(1) −0·051

Plane (g): C(13) −0·021, C(14) 0·022, X(4,5) * 0·027 X(6,7) * −0·027, Fe 0·521

* X(4,5) and X(6,7) are the midpoints of the C(4)—C(5) and C(6)—C(7) bonds.

difference between the complex and uncomplexed azepine rings is the greater planarity about the nitrogen atom in the complexes; in N-p-bromobenzenesulphonyl-azepine [7] and N-phenoxycarbonylazepine [8] the nitrogen atom is displaced by 0·22 and 0·13 Å, respectively, from the plane defined by the atoms bound to nitrogen, whereas in (N-methoxycarbonylazepine)tricarbonyliron [10] and (3-formyl-N-ethoxycarbonylazepine)tricarbonyliron the corresponding displacements are only 0·020 and 0·006 Å,

indicating a much closer approximation to sp^2 hybridization for the nitrogen atom in the complexes. The N–C(2) bond in a complexed azepine ring is consistently shorter than the N–C(7) bond, e.g., 1·343 and 1·391 Å in (3-acetyl-1H-azepine)tricarbonyliron,[11] and introduction of an unsaturated exocyclic N-substituent results in a significant lengthening of both N–C ring bonds, cf. 1·379 and 1·447 Å in (2). These results are consistent with competing conjugative interactions leading to the extensive delocalization of the nitrogen ' lone pair '.

When the molecule is viewed in projection on to the C(4), C(5), C(6), C(7)-butadiene plane, two of the carbonyl ligands eclipse the outer carbon–carbon bonds of the
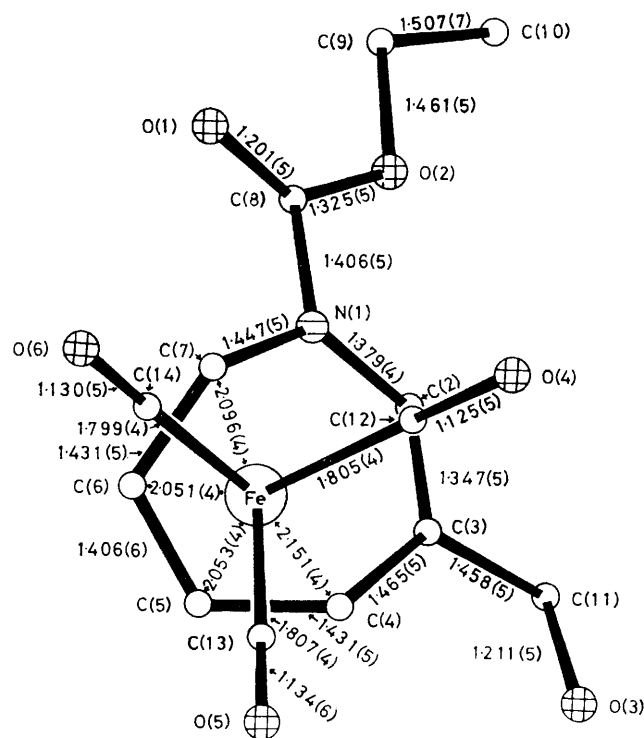

FIGURE 3   Projection of the molecular structure on to the plane defined by C(4), C(5), C(6), and C(7)

TABLE 6

The C–H bond lengths (Å)

C(2)–H(2)	0·95(3)	C(9)–H(9a)	1·10(5)
C(4)–H(4)	0·96(3)	C(9)–H(9b)	0·89(5)
C(5)–H(5)	0·95(5)	C(10)–H(10a)	0·88(7)
C(6)–H(6)	0·92(4)	C(10)–H(10b)	0·87(6)
C(7)–H(7)	0·93(3)	C(10)–H(10c)	1·06(7)
C(11)–H(11)	1·04(4)		

diene (Figure 3), a standard arrangement in dienetricarbonyliron complexes. The co-ordination of the iron atom may be described as distorted square pyramidal with the iron atom 0·52 Å above the plane through the carbonyl carbon atoms C(13) and C(14) and the midpoints of the C(4)—C(5) and C(6)—C(7) bonds. The non-equivalence of basal and apical carbonyl groups is not reflected in the Fe–CO bond lengths but is apparent, however, in the angle between the basal Fe–CO bonds, 93·4°, being

significantly smaller than the angles between basal and apical bonds, 99·8 and 100·3°.

The C–H bond lengths range from 0·87 to 1·10 Å (see Table 6) with a mean of 0·96 Å. The contraction from expected internuclear separations of ca. 1·07 Å has been noted in other X-ray studies and has been attributed to the displacement of the hydrogen electron density towards the carbon atom on bond formation.

EXPERIMENTAL

Crystal Data.—(3-Formyl-N-ethoxycarbonylazepine)tricarbonyliron, $C_{13}H_{11}FeNO_6$, $M = 333·0$, Triclinic, $a = 7·022(3)$, $b = 10·550(4)$, $c = 9·500(3)$ Å, $\alpha = 92°\ 49(2)'$, $\beta = 94°\ 32(2)'$, $\gamma = 96°\ 8(2)'$, $U = 696·4$ Å³, $D_m = 1·58$, $Z = 2$, $D_c = 1·587$, $F(000) = 340$. Space group $P\bar{1}$. Mo-K_α radiation, $\lambda = 0·7107$ Å, $\mu = 11·5$ cm⁻¹.

Crystallographic Measurements.—Preliminary values of the cell dimensions were obtained from precession photographs of a crystal with dimensions $0·10 \times 0·35 \times 0·50$ mm³. The cell parameters were subsequently adjusted by a least-squares treatment of the θ, χ, and φ setting angles of a number of reflections measured on a Hilger and Watts Y290 automatic diffractometer with Mo-K_α radiation. The intensity measurements were made by the θ—2θ step scan procedure, each reflection being scanned in 80 equal steps from 0·8° below to 0·8° above $2\theta_{calc}$. Each step was scanned 1 s and background counts were taken at each end of the total range for 20 s. The intensities of two standard reflections were monitored after every 40 reflections and only small random fluctuations noted. Intensities were collected for reflections with h positive within θ(Mo-K_α) $\leqslant$ 25°. The scan counts (P) and the background counts (B_1, B_2) were combined to yield the integrated intensity $I = P - 2(B_1 + B_2)$. Intensities were corrected for Lorentz-polarization effects, but absorption was neglected. In all, 2467 independent values of $|F_o|$ were obtained and when reflections with $P < 2(B_1 + B_2)$ were eliminated 2363 values remained.

Structure Analysis.—The initial co-ordinates of the iron atom were deduced from the three-dimensional Patterson synthesis and the positions of the carbon, nitrogen, and oxygen atoms were then obtained from a three-dimensional electron-density distribution phased by the iron atom (R 46%).

Accurate atomic parameters were derived by a series of least-squares calculations with the programme developed by D. W. J. Cruickshank, J. G. F. Smith, and J. G. Sime for the KDF 9 computer at Glasgow University. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where w is a weight given by the expression: $w = [1 - \exp\{-p_1(\sin \theta/\lambda)^2\}][1 + p_2|F_o| + p_3|F_o|^2]$. The values of p_1, p_2, and p_3 were adjusted at several stages to ensure approximate constancy of $\langle w\Delta^2 \rangle$ over various ranges of $|F_o|$ and sin θ, and the final values employed were 50·0, 0·1, and 0·001, respectively. The scattering factors used in the analysis were taken from ref. 15 and the values for iron were corrected for dispersion.

Two cycles of full-matrix refinement with isotropic thermal parameters reduced R to 10·6%. The atoms were then assigned anisotropic thermal parameters and a block diagonal procedure employed; two rounds of calculations gave R 6·2%. A difference electron-density distribution enabled all the hydrogen atoms to be located unambiguously,

15 ' International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

the average peak height being 0.6 eÅ^{-3}. The hydrogen atoms were then included in the least-squares calculations

with isotropic thermal parameters and after four rounds of calculations convergence was reached at R 4.6%.*