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Crystal structure of the low-melting form of ferrocenecarboxaldoxime

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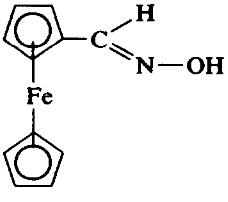
Abstract

An X-ray diffraction study shows that in the crystal of the low melting form of ferrocenecarboxaldoxime, $(C_5H_5)Fe(C_5H_4CH{=}NOH)$ there are two molecular sites in the asymmetric unit, and both sites contain a disordered mixture of *E* and *Z* geometrical isomers. There are no close contacts between the iron atom and the hydroxyl group of the oxime substituent, but there is extensive intermolecular hydrogen bonding.

Introduction

Ferrocenecarboxaldoxime, $(C_5H_5)Fe(C_5H_4CH{=}NOH)$, has been reported [1] to exist in two crystalline modifications, denoted α, m.p. 96–99 °C and β, m.p. 155–157 °C. These two forms have been tentatively assigned the *E* and *Z* configurations **1** and **2** respectively, although there is little evidence to support this.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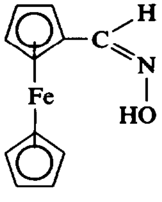
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Here we report a crystallographic study of the low-melting form, which is revealed by X-ray structure analysis to contain both *E* and *Z* isomers, co-existing as disordered occupants of common molecular sites.

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Experimental

The carboxaldoxime was prepared from ferrocene via *N*,*N*-dimethylaminoferrocene, ferrocenylcarbinol, and ferrocene carboxaldehyde [2]: the oxime was prepared under basic conditions, m.p. 97–98 °C (lit: 96–99 °C [1]), found C, 58.1; H, 5.0; N, 5.9. $C_{11}H_{11}FeNO$ calcd.: C, 57.7; H, 4.8; N, 6.1%. For purposes of identification, the oxime was also converted into the corresponding nitrile [1], m.p. 106–108 °C (lit: 107–108 °C [1]), found C, 62.8; H, 4.3: N, 6.7. $C_{11}H_9FeN$ calcd.: 62.6; H, 4.3; N, 6.6%; and into the oxime acetate [2], m.p. 80–81 °C (lit: 80–81 °C [2]), found C, 57.5; H, 4.8; N, 5.1. $C_{13}H_{13}FeNO_2$ calcd.: C, 57.6; H, 4.8; N, 5.2%.

Spectroscopic data

Ferrocenecarboxaldoxime: NMR ($CDCl_3$), δ_H 4.19 (s, 5H, C_5H_5), 4.33 (m, 2H) and 4.55 (m, 2H) (C_5H_4), 8.01 (s, 1H, = C(H)), 9.5 (br, s, 2H, NOH); δ_c 67.6(d), 70.0(d) 76.1(s) (C_5H_4), 69.2(d) (C_5H_5), 149.9(d), ($=C\langle$), IR (CH_2Cl_2), 3570 and 3271, ν(OH); 1656, ν(C=N). Mass spectrum m/z 229 $(M)^+$, 211 $(M-H_2O)^+$, 185 $(M-CH_2NO)^+$, 164 $(M-C_5H_5)^+$, 146 $(M-C_5H_5-H_2O)^+$, 138 $(C_5H_5Fe\text{-}OH)^+$, 121 $(C_5H_5Fe)^+$.

X-ray crystallography

Crystals suitable for X-ray examination were grown from solutions in CH_2Cl_2/ light petroleum.

Crystal data

$C_{11}H_{11}FeNO$, $M = 229.06$, monoclinic, $a = 26.512(6)$, $b = 12.798(4)$, $c = 12.855(2)$ Å, $\beta = 114.37(1)°$, $V = 3973(3)$ Å^3, $Z = 16$, $D_c = 1.53$ g cm^{-3}, μ(Mo-K_α) = 14.8 cm^{-1}, $\lambda = 0.71073$Å, $F(000) = 1888$,. Systematic absences; $h0l$ absent if $l = 2n + 1$, hkl absent if $h + k = 2n + 1$ allow the space group to be either $C2/c$ or Cc: the former was chosen and confirmed by the successful refinement.

Data collection

A crystal of dimensions 0.06 × 0.54 × 0.58 mm was used. Cell dimensions were determined by least-squares refinement using the setting angles of 25 reflections in the range $9 \leq \theta \leq 15°$. Intensity data were collected at 21 °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation in the ω–2θ scan mode; ω-scan rate 1–7° min^{-1}; ω-scan width $(0.70 + 0.335 \tan\theta)°$; the maximum value of 2θ was 54°. 4671 reflections were measured, of which 1768 were unique and not systematically absent, and 1762 had $F \geq 3\sigma(F)$. Lorentz and polarisation corrections were applied, together with a numerical absorption correction for which the maximum and minimum transmission coefficents were 0.921 and 0.542, and an anisotropic decay correction for which the correction factors on I ranged from 0.972 to 1.104 with mean 1.041.

Structure solution and refinement

The structure was solved using the Patterson heavy atom method, which allowed us to locate the positions of the two non-equivalent iron atoms. The remaining atoms were located in succeeding difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were in-

Table 1

Positional and thermal parameters and their e.s.d.'s [a]

Atom	x	y	z	$B(\text{Å}^2)$
Fe1	0.07592(4)	0.17487(7)	0.55583(7)	4.81(2)
Fe2	0.17273(4)	0.68270(8)	0.61094(9)	6.51(3)
C1	0.1056(3)	0.1463(6)	0.4370(5)	5.9(2)
C2	0.0634(3)	0.0715(5)	0.4280(5)	6.3(2)
C3	0.0142(3)	0.1296(6)	0.4047(6)	7.3(2)
C4	0.0256(3)	0.2321(6)	0.3987(6)	7.9(2)
C5	0.0805(3)	0.2433(6)	0.4183(5)	6.9(2)
C6	0.1633(3)	0.1143(6)	0.4689(5)	6.8(2)
C11	0.1419(3)	0.1855(7)	0.7078(6)	7.2(2)
C12	0.1101(3)	0.0998(6)	0.7071(5)	7.6(2)
C13	0.0580(3)	0.1385(7)	0.6897(6)	8.7(2)
C14	0.0571(3)	0.2412(7)	0.6786(6)	8.3(2)
C15	0.1090(3)	0.2727(6)	0.6894(6)	7.8(2)
C21	0.1340(4)	0.5465(6)	0.5508(7)	9.4(3)
C22	0.1486(5)	0.5558(7)	0.670(1)	14.2(4)
C23	0.2113(5)	0.5659(8)	0.7203(9)	14.0(5)
C24	0.2226(4)	0.5571(7)	0.627(1)	15.7(4)
C25	0.1754(5)	0.5534(7)	0.5146(9)	15.6(3)
C26	0.0666(6)	0.5406(10)	0.4710(13)	7.4(4)
C31	0.1193(3)	0.8047(6)	0.5515(7)	7.8(2)
C32	0.1456(4)	0.8100(6)	0.6659(7)	8.3(2)
C33	0.2024(4)	0.8164(6)	0.6998(6)	7.6(2)
C34	0.2126(3)	0.8157(6)	0.6033(7)	7.7(2)
C35	0.1601(4)	0.8070(6)	0.5083(6)	8.5(3)
O1	0.2558(3)	0.1244(7)	0.5172(8)	8.6(2)
O1 ★	0.1876(5)	0.2874(10)	0.4747(10)	8.2(4)
N1	0.2030(2)	0.1758(5)	0.4819(4)	6.9(2)
O2	0.0684(6)	0.5050(10)	0.3070(16)	10.5(5)
N2	0.0507(8)	0.5212(10)	0.3762(11)	6.6(5)
O2 ★	0.0	0.5	0.5	4.8(8)
N2 ★	0.0525(15)	0.5302(24)	0.5557(42)	8(1)

[a] Occupancy factors for C26, O1, O1 ★, O2, N2, O2 ★ and N2 ★ were 0.47, 0.59, 0.41, 0.33, 0.33, 0.14, 0.14 respectively. This allowed for the disorder of the OH group in molecule **A**, and the partial occupancy and disorder of the CH=NOH group in molecule **B**. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)\cdot[a^2\cdot B_{1,1} + b^2\cdot B_{2,2} + c^2\cdot B_{3,3} + ab(\cos\gamma)\cdot B_{1,2} + ac(\cos\beta)\cdot B_{1,3} + bc(\cos\alpha)\cdot B_{2,3}]$.

cluded in the refinement, but were restrained to ride on the atom to which they are bonded, with $d(\text{C–H}) = 0.95$ Å and fixed isotropic thermal parameters. A secondary extinction coefficient [3] refined to 1.0×10^{-6}; the final R values were R, 0.054; R_w, 0.079.

Scattering factors were taken from Cromer and Waber [4]: anomalous dispersion effects were included in F_c [5], and values of f' and f'' were those of Cromer [5]. All calculations were performed on a PDP-11/73 computer using SDP-PLUS [7].

Final refined atom coordinates are given in Table 1, and selected bond lengths and angles in Table 2. Perspective views of molecules **A** and **B** of the asymmetric unit, showing also the atom-numbering scheme, are in Figs. 1 and 2.

Tables of hydrogen-atom coordinates, anisotropic temperature factors, and torsional angles have been deposited at the Cambridge Crystallographic Data Centre,

Table 2

Molecular dimensions

(a) Interatomic distances (Å)

Fe1-C1	2.020(8)	Fe2-C34	2.028(8)	C23-C24	1.351(20)
Fe1-C2	2.028(7)	Fe2-C35	2.004(7)	C24-C25	1.473(14)
Fe1-C3	2.040(6)	C1-C2	1.441(10)	C26-N2	1.141(21)
Fe1-C4	2.043(7)	C1-C5	1.382(10)	C26-N2*	1.30(6)
Fe1-C5	2.020(8)	C1-C6	1.468(10)	C31-C32	1.344(11)
Fe1-C11	2.019(6)	C2-C3	1.422(11)	C31-C35	1.405(15)
Fe1-C12	2.018(6)	C3-C4	1.354(12)	C32-C33	1.386(13)
Fe1-C13	2.020(9)	C4-C5	1.378(12)	C33-C34	1.375(13)
Fe1-C14	2.028(9)	C6-N1	1.269(10)	C34-C35	1.427(10)
Fe1-C15	2.010(7)	C11-C12	1.381(12)	O1-N1	1.438(10)
Fe2-C21	2.009(8)	C11-C15	1.376(11)	O1*-N1	1.478(14)
Fe2-C22	2.006(12)	C12-C13	1.396(12)	O2-N2	1.18(3)
Fe2-C23	2.018(10)	C13-C14	1.322(12)	O2*-N2*	1.33(3)
Fe2-C24	2.036(10)	C14-C15	1.384(13)	O1···N1(I)	2.779(11)
Fe2-C25	2.086(11)	C21-C22	1.422(15)	O1*···N1(I)	2.759(15)
Fe2-C31	2.033(8)	C21-C25	1.362(19)	O2···N2*(II)	3.11(6)
Fe2-C32	2.022(9)	C21-C26	1.655(16)	O2···N2(III)	3.070(21)
Fe2-C33	2.027(7)	C22-C23	1.521(18)		

(b) Bond angles (°)

C1-Fe1-C2	41.7(3)	C1-C6-N1	125.1(7)
C1-Fe1-C3	68.8(3)	Fe1-C11-C12	69.9(4)
C1-Fe1-C4	67.5(3)	Fe1-C11-C15	69.7(4)
C1-Fe1-C5	40.0(3)	C12-C11-C15	107.4(7)
C2-Fe1-C3	40.9(3)	Fe1-C12-C11	70.1(4)
C2-Fe1-C4	67.1(3)	Fe1-C12-C13	69.9(4)
C2-Fe1-C5	67.8(3)	C11-C12-C13	106.3(7)
C3-Fe1-C4	38.7(3)	Fe1-C13-C12	69.7(5)
C3-Fe1-C5	66.6(3)	Fe1-C13-C14	71.3(5)
C4-Fe1-C5	39.7(3)	C12-C13-C14	110.1(8)
C11-Fe1-C12	40.0(3)	Fe1-C14-C13	70.6(5)
C11-Fe1-C13	66.8(3)	Fe1-C14-C15	69.3(5)
C11-Fe1-C14	67.2(3)	C13-C14-C15	107.7(8)
C11-Fe1-C15	39.9(3)	Fe1-C15-C11	70.4(4)
C12-Fe1-C13	40.5(4)	Fe1-C15-C14	70.7(4)
C12-Fe1-C14	66.8(3)	C11-C15-C14	108.5(7)
C12-Fe1-C15	67.0(3)	Fe2-C21-C22	69.1(5)
C13-Fe1-C14	38.1(4)	Fe2-C21-C25	73.7(6)
C13-Fe1-C15	65.7(3)	Fe2-C21-C26	121.9(6)
C14-Fe1-C15	40.1(4)	C22-C21-C25	117.6(9)
C21-Fe2-C22	41.5(4)	C22-C21-C26	115(1)
C21-Fe2-C23	70.0(4)	C25-C21-C26	128(1)
C21-Fe2-C24	64.0(4)	Fe2-C22-C21	69.4(6)
C21-Fe2-C25	38.8(5)	Fe2-C22-C23	68.2(6)
C22-Fe2-C23	44.4(5)	C21-C22-C23	103(1)
C22-Fe2-C24	67.4(5)	Fe2-C23-C22	67.4(6)
C22-Fe2-C25	71.1(5)	Fe2-C23-C24	71.3(6)
C23-Fe2-C24	38.9(6)	C22-C23-C24	102.6(9)
C23-Fe2-C25	72.2(4)	Fe2-C24-C23	69.8(7)
C24-Fe2-C25	41.9(4)	Fe2-C24-C25	70.9(6)
C31-Fe2-C32	38.7(3)	C23-C24-C25	118(1)
C31-Fe2-C33	67.2(3)	Fe2-C25-C21	67.6(6)

Table 2 (continued)

(b) Bond angles (°)			
C31–Fe2–C34	68.5(3)	Fe2–C25–C24	67.3(6)
C31–Fe2–C35	40.7(4)	C21–C25–C24	98(1)
C32–Fe2–C33	40.0(4)	C21–C26–N2	120(2)
C32–Fe2–C34	66.9(4)	C21–C26–N2 *	96(2)
C32–Fe2–C35	66.7(4)	N2–C26–N2 *	140(2)
C33–Fe2–C34	39.6(4)	Fe2–C31–C32	70.2(5)
C33–Fe2–C35	67.8(3)	Fe2–C31–C35	68.6(4)
C34–Fe2–C35	41.5(3)	C32–C31–C35	107.1(7)
Fe1–C1–C2	69.4(4)	Fe2–C32–C31	71.1(5)
Fe1–C1–C5	70.0(5)	Fe2–C32–C33	70.2(5)
Fe1–C1–C6	121.7(4)	C31–C32–C33	110.6(9)
C2–C1–C5	106.2(6)	Fe2–C33–C32	69.8(5)
C2–C1–C6	121.4(6)	Fe2–C33–C34	70.2(4)
C5–C1–C6	132.2(7)	C32–C33–C34	108.0(6)
Fe1–C2–C1	68.9(4)	Fe2–C34–C33	70.2(5)
Fe1–C2–C3	70.0(4)	Fe2–C34–C35	68.4(5)
C1–C2–C3	106.5(6)	C33–C34–C35	106.6(8)
Fe1–C3–C2	69.1(3)	Fe2–C35–C31	70.7(5)
Fe1–C3–C4	70.7(4)	Fe2–C35–C34	70.2(4)
C2–C3–C4	108.2(7)	C31–C35–C34	107.6(7)
Fe1–C4–C3	70.5(4)	C6–N1–O1	113.8(6)
Fe1–C4–C5	69.3(4)	C6–N1–O1 *	113.3(8)
C3–C4–C5	109.4(7)	O1–N1–O1 *	132.1(7)
Fe1–C5–C1	70.0(4)	C26–N2–O2	139(2)
Fe1–C5–C4	71.1(5)	C26–N2 * –O2 *	100(3)
C1–C5–C4	109.7(7)		

The roman numerals refer to the following equivalent positions:

(I) $1/2-x, 1/2-y, 1-z$.

(II) $x, 1-y, -1/2+z$.

(III) $-x, y, 1/2-z$.

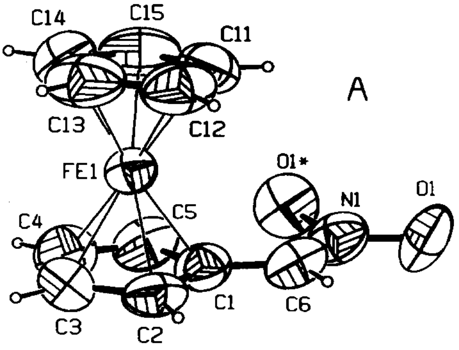


Fig. 1. Perspective view of the ferrocenecarboxaldoxime molecule as found in sites **A**, showing the atom-numbering scheme, and the *E*, *Z* disorder.

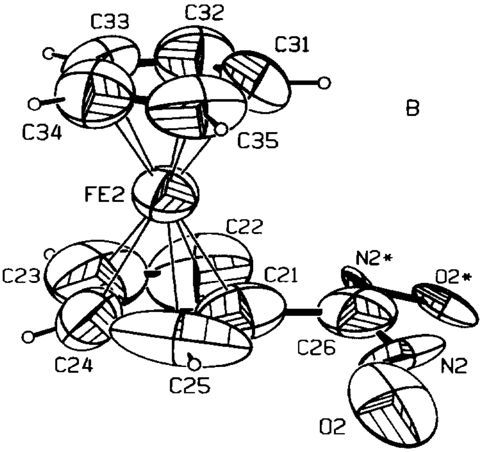


Fig. 2. Perspective view of the ferrocenecarboxaldoxime molecule as found in sites **B**, showing the atom-numbering scheme, and the rotational and *E*, *Z* disorder.

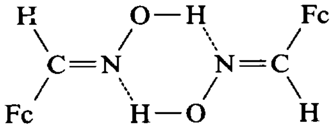
and tables of observed and calculated structure factors are available from the authors.

Results and discussion

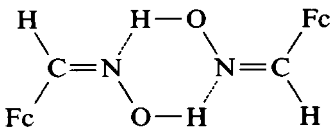
The unit-cell dimensions and the space-group demand that the asymmetric unit contains two molecules, in sites hereafter designated as **A** and **B**.

In sites **A**, the molecules exhibit disorder resulting from the presence of a mixture of *E* and *Z* isomers. Refinement of the occupancy factors for the oxygen atoms in the two alternative sites showed that 59% of the molecules in sites **A** have the *E* configuration while 41% have the *Z* configuration. The whole, disordered, C(H)=NOH group is effectively coplanar with the adjacent cyclopentadiene ring, the two C–C–N–O dihedral angles being 6.6(10) and 177.9(6)°. Within the ferrocenyl fragment, the mean Fe–C distances for the two independent rings are identical within experimental uncertainty, but the mean C–C distance in the unsubstituted ring is marginally shorter than that in the substituted ring: this phenomenon has been noted previously [8]. The cyclopentadiene rings are twisted by 11.3° from the fully eclipsed conformation.

Pairs of site **A** molecules are related by a centre of inversion and are joined by weak hydrogen bonds: because of the *E*, *Z* disorder the net effect is the superimposition of 59% site occupancy by the *E* molecules, in pairs (**3**) upon 41% site occupancy by pairs of *Z* molecules, [Fc = (C_5H_5)Fe(C_5H_4)] (**4**).

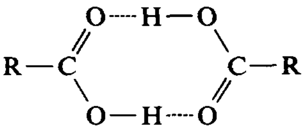


(**3**)



(**4**)

This pattern of hydrogen bonding resembles that widely found in carboxylic acid dimers $(RCOOH)_2$ (5), but having a six-membered ring rather than the eight-membered ring in (5).


(5)

The hydrogen bond distances N · · · O are 2.78(1) Å in **3**, and 2.76(2) Å in **4**, both significantly shorter than the sum 3.05 Å of the Van der Waals' radii [9]. The structural data and the infrared spectrum both show that the hydrogen bonds are weak.

While the isolated monomers **1** and **2** of the *E* and *Z* isomers respectively are significantly different from one another, the dimers **3** and **4**, based upon a common ring as the molecular core, are extremely similar in overall molecular shape and polarity: this, no doubt, contributes significantly to the existence of both isomers in the disordered form revealed by the X-ray analysis.

The molecules in sites **B** exhibit a more complex form of disorder. Firstly, refinement of the site occupancies for the C(H)=NOH fragment showed that only 47% of the site **B** molecules are in fact Fc–C(H)=NOH, the other 53% being unsubstituted ferrocene; secondly, the molecules exhibit *E*, *Z* disorder as for the site **A** molecules, but now with 30% of the oxime molecules having the *E* configuration and 70% the *Z* configuration; thirdly, there is disorder caused by rotation about the exocyclic carbon–carbon bond, C21–C26; the best fit of the X-ray data was found with one rotamer having all *E* configuration, and the other rotamer all *Z*. The hydrogen bonding involving the oxime molecules in site **B** is also more complex than that for the **A** site molecules. One set of hydrogen bonds connects molecules related by the *c* glideplane, with N · · · O distances of 3.11(6) Å, and another set of hydrogen bonds connects molecules related by the two-fold rotation axis, with N · · · O distances of 3.07(2) Å: all of these hydrogen bonds are very weak.

For the oxime substituents in site **A**, the C=N bond length, 1.269(10) Å is typical of that found in oximes [10], but the N–O distances, 1.438(10) Å in the *E* isomer and 1.478(14) Å in the *Z* isomer, are both significantly in excess of the upper quartile values, 1.401 Å for a sample of twenty carboxaldoximes and 1.408 Å for a sample of 67 oximes of all types [10]. The multiple disorder found for site **B** precludes meaningful comparisons of structural data.

The structural results above were obtained from a sample of ferrocenecarboxaldoxime which was chromatographically homogeneous and apparently analytically pure, and which moreover provided two analytically pure derivatives, the nitrile and the oxime acetate. They show that the characterisation of the isomeric forms of ferrocenecarboxaldoxime by the use of simple physical properties such as melting point is not secure, and that both *E* and *Z* isomers can co-exist in a single crystal.

Neither site **A** nor site **B** molecules of the oxime show any close contacts between the iron atom in the ferrocene nucleus, and the hydroxyl group of the oxime fragment: there are no structural features which could explain the very ready dehydration of the oxime to the nitrile.

Acknowledgements

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