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The crystal structure of (5-methyl-1,2,4-oxadiazol-3-yl)ferrocene, $C_{13}H_{12}FeN_2O$

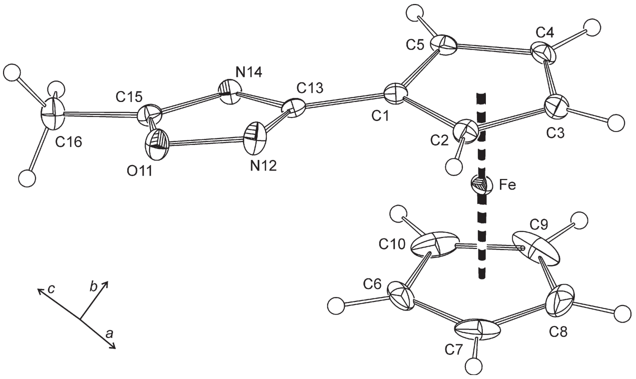

Table 1: Data collection and handling.

Crystal:	Orange bar
Size:	$0.68 \times 0.14 \times 0.12$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	13.3 cm^{-1}
Diffractometer, scan mode:	Bruker APEXII CCD, φ and ω
$2\theta_{max}$, completeness:	54.8°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8213, 2542, 0.023
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2190
$N(param)_{refined}$:	155
Programs:	SHELX [1], Bruker [2–4], Platon [5]

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Abstract

$C_{13}H_{12}FeN_2O$, monoclinic, $P2_1/n$ (no. 14), $a = 5.9035(2)$ Å, $b = 20.7111(6)$ Å, $c = 9.1403(3)$ Å, $\beta = 90.0762(16)°$, $V = 1117.57(6)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0282$, $wR_{ref}(F^2) = 0.0656$, $T = 150(2)$ K.

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The crystal structure is shown in the figure. Table 1 contains measurement conditions. Table 2 lists the atoms along with their coordinates and displacement parameters.

Source of material

Under an argon atmosphere, a solution of sodium ethoxide freshly prepared by dissolving sodium metal (230 mg, 10 mmol) in absolute ethanol (10 mL) was added to solid hydroxylamine hydrochloride (690 mg, 10 mmol). The formed precipitate (NaCl) was filtered off and the clear filtrate containing NH_2OH was added to a suspension of cyanoferrocene (422 mg, 2.0 mmol) [6] in absolute ethanol (5 mL). The resultant mixture was heated under reflux for 4 h and then concentrated to ca. 4 mL by evaporation under vacuum. The residue was partitioned between ethyl acetate and 0.3 M aqueous HCl (30 mL each). The orange organic phase was separated, dried over $MgSO_4$ and evaporated, leaving a solid residue, which was purified by chromatography on a silica gel column with ethyl acetate–hexane mixture (3:1) as the eluent. Unreacted cyanoferrocene (101 mg, 24%) was eluted first, followed by the title compound (139 mg, 26%) and, finally, ferrocenecarboxamide (137 mg, 28%).

Characterization data for the title compound. **^{1}H NMR** (399.95 MHz, $CDCl_3$): δ 2.62 (s, 3 H, CH_3), 4.15 (s, 5 H, C_5H_5), 4.43 and 4.89 (2 × virtual t, $J = 1.7$ Hz, 2 H, C_5H_4). **^{13}C{^{1}H} NMR** (100.58 MHz, $CDCl_3$): δ 12.35 (CH_3), 68.20 (CH of C_5H_4), 69.83 (C_5H_5), 69.97 (C_{ipso} of C_5H_4), 70.39 (CH of C_5H_4), 170.14 and 175.82 (2 × C_{ipso} of oxadiazole). **ESI MS+:** m/z 268 (M^+), 291 ($[M + Na]^+$). Single-crystals were grown from hot n-heptane.

Experimental details

Hydrogen atoms were included in their calculated positions as refined as riding atoms (AFIX 43 and 137 for the aromatic and CH_3 hydrogens, respectively, in the SHELXL-97 program [1]). The U_{iso} of the hydrogen atoms were constrained to a multiple of U_{eq} of their bonding carbon atoms (1.2-times for the aromatic CH and 1.5-times for the methyl protons).

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Fe	0.98415(4)	0.160763(11)	0.13905(3)	0.01745(9)
C1	1.0151(3)	0.17589(8)	0.35737(18)	0.0180(3)
C2	1.2316(3)	0.18226(9)	0.28822(19)	0.0208(4)
H2	1.3632	0.1575	0.3091	0.025*
C3	1.2134(3)	0.23242(9)	0.1825(2)	0.0243(4)
H3	1.3312	0.2468	0.1198	0.029*
C4	0.9891(3)	0.25736(9)	0.1866(2)	0.0237(4)
H4	0.9316	0.2914	0.1275	0.028*
C5	0.8658(3)	0.22260(8)	0.29448(19)	0.0204(4)
H5	0.7117	0.2292	0.3201	0.025*
C6	0.8829(4)	0.06782(9)	0.1095(2)	0.0329(5)
H6	0.8669	0.0363	0.1842	0.039*
C7	1.0767(4)	0.07920(11)	0.0292(3)	0.0417(6)
H7	1.2160	0.0567	0.0396	0.050*
C8	1.0356(6)	0.12834(13)	−0.0680(3)	0.0570(8)
H8	1.1414	0.1457	−0.1357	0.068*
C9	0.8129(6)	0.14828(11)	−0.0505(3)	0.0623(10)
H9	0.7391	0.1814	−0.1043	0.075*
C10	0.7148(4)	0.11026(12)	0.0626(3)	0.0433(6)
H10	0.5644	0.1132	0.0989	0.052*
O11	0.9829(2)	0.05233(6)	0.62557(14)	0.0247(3)
N12	1.1115(3)	0.09436(8)	0.53576(17)	0.0254(4)
C13	0.9566(3)	0.12731(8)	0.46631(18)	0.0167(3)
N14	0.7366(2)	0.11164(7)	0.50355(16)	0.0195(3)
C15	0.7643(3)	0.06643(8)	0.59945(19)	0.0189(4)
C16	0.5931(3)	0.02923(10)	0.6823(2)	0.0269(4)
H16A	0.4412	0.0445	0.6563	0.040*
H16B	0.6182	0.0352	0.7874	0.040*
H16C	0.6066	−0.0167	0.6579	0.040*

Discussion

(5-Methyl-1,2,4-oxadiazol-3-yl)ferrocene was isolated serendipitously during an attempted preparation of ferrocenecarboxamide oxime by a modified literature procedure [7]. It appears likely that in our hands the originally targeted compound underwent an acid-catalyzed condensation with ethyl acetate used during the work-up to afford the title compound. Previously, this oxadiazole was obtained by the reaction of (ferrocenylmethyl)trimethylammonium iodide with sodium nitrite in refluxing acetonitrile [8].

The title compound crystallizes with one molecule per asymmetric unit. Its structure comprises a regular ferrocene moiety showing similar Fe—C distances (2.021(3)–2.0475(19) Å) and, consequently, practically negligible tilting of the cyclopentadienyl rings (dihedral angle: 1.31(13)°) that assume an approximate eclipsed conformation. Carbon atoms in the unsubstituted cyclopentadienyl ring exhibit large displacement parameters which, however, corresponds with a low barrier of the rotation of the cyclopentadienyl rings in ferrocene [9] and also with an absence of intermolecular interactions that could possibly control molecular conformation in the solid state.

The 1,2,4-oxadiazole moiety in the structure appears rotated with respect to its bonding cyclopentadienyl ring C(1—5) by 15.23(10)° but otherwise remains planar (the maximum deviation of the ring-forming atoms from the mean plane does not exceed 0.005 Å). The formal double bonds in the oxadiazole ring N12—C13 (1.305(2) Å) and N14—C15 (1.293(2) Å) are considerably shorter than the three remaining bonds [O11—N12 1.418(2) Å, C13—N14 1.382(2) Å, and C15—O11 1.344(2) Å], which in turn suggests a partly localized character of the oxadiazole moiety. Furthermore, the in-ring angles are all near the value expected for a regular pentagon (108°). Yet, they can be divided into two distinct groups: three angles at the heteroatoms that are more acute than the ideal value [C13—N14—C15 102.65(13)° $<$ O11—N12—C13 103.14(15)° $<$ N12—O11—C15 106.17(13)°], and two more opened angles associated with the carbon atoms [O11—C15—N14 113.47(15)° $<$ N12—C13—N14 114.56(15)°]. Similar features can be found in the molecular structures of the related compounds such as 5-methyl-3-(4-nitrophenyl)-1,2,4-oxadiazole [10], 3-*tert*-butyl-5-(4-nitrophenyl)-1,2,4-oxadiazole and 5-(4-aminophenyl)-3-*tert*-butyl-1,2,4-oxadiazole [11], and 5-chloromethyl-3-(4-methylphenyl)-1,2,4-oxadiazole [12].

The C1–C13 bond connecting the two molecular parts is rather short (1.457(2) Å), suggesting that the conjugation of the ferrocene unit with the attached heterocyclic moiety is not disrupted. This distance is shorter than that in ferrocencarboxamide (1.483(2) and 1.491(2) Å for two different polymorphs) [13] but compares well with the value determined for ferrocenecarboxylic acid (1.462(2) Å at 173 K) [14].

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