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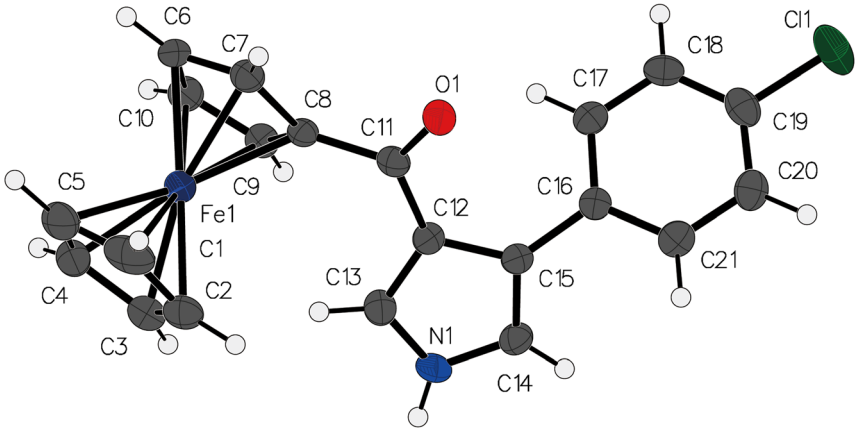
Crystal structure of (4-(4-chlorophenyl)-1*H*-pyrrole-3-carbonyl)ferrocene, $C_{21}H_{16}ClFeNO$



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Abstract

$C_{21}H_{16}ClFeNO$, monoclinic, $P2_1/c$ (no. 14), a = 14.6936(11) Å, b = 9.3784(6) Å, c = 12.7854(8) Å, β = 105.183(2)°, V = 1700.4(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.0584 w$R_{ref}(F^2)$ = 0.1719, T = 170 K.

CCDC no.: 2314040

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.11 × 0.09 × 0.05 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.05 mm^{-1}
Diffractometer, scan mode:	Bruker D8 VENTURE, φ and ω scans
θ_{max}, completeness:	26.6°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12549, 3530, 0.068
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2,456
$N(param)_{refined}$:	226
Programs:	Bruker,[1] SHELX[2,3]

1 Source of materials

To a solution of 1–ferrocenyl-3-(4-chlorophenyl)-2-propen-1-one (3.50 g, 10 mmol) and tosylmethyl isocyanide (2.15 g, 11 mmol) in N,N-dimethylformamide (25 mL) was added potassium tert-butoxide (2.24 g, 20 mmol). The mixture was stirred at room temperature for 12 h, until the TLC indicated the reaction was completed. The mixture was diluted with brine, and then extracted with ethyl acetate (3 × 30 mL). The organic phase was washed with brine (30 mL), dried with anhydrous sodium sulphate, and then concentrated under pressure. The title compound was separated by silica-gel column chromatography with ethyl acetate-petroleum ether (25 %) gradient solvent system. The target product was obtained as a white solid. Yield: 68.5 %. For crystal growth, the product was dissolved in a minimal amount of hot ethanol and slowly cooled to room temperature (Tables 1 and 2).

2 Experimental details

The crystal structure was solved via Direct Methods using the SHELXT program[2] and refined through full-matrix least squares on F^2 using SHELXL.[3] Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically idealized positions and refined using a riding model.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Fe1	0.12689 (4)	0.40872 (7)	0.37890 (5)	0.0275 (2)
Cl1	0.77898 (10)	0.45575 (17)	0.95474 (11)	0.0551 (4)
O1	0.3348 (2)	0.3562 (4)	0.6660 (2)	0.0292 (7)
N1	0.4420 (2)	0.1944 (4)	0.3871 (3)	0.0288 (9)
H1	0.443510	0.153855	0.325523	0.035*
C1	0.0440 (4)	0.2318 (6)	0.3689 (5)	0.0493 (15)
H1A	0.026590	0.186904	0.427362	0.059*
C2	0.1244 (3)	0.1991 (5)	0.3319 (4)	0.0372 (11)
H2	0.170527	0.128743	0.361498	0.045*
C3	0.1241 (3)	0.2890 (5)	0.2436 (4)	0.0371 (11)
H3	0.169694	0.289950	0.202884	0.045*
C4	0.0438 (4)	0.3776 (6)	0.2263 (4)	0.0480 (15)
H4	0.026161	0.448650	0.171817	0.058*
C5	−0.0059 (3)	0.3429 (7)	0.3036 (5)	0.0555 (17)
H5	−0.062492	0.386282	0.310524	0.067*
C6	0.1058 (3)	0.5863 (5)	0.4622 (4)	0.0297 (10)
H6	0.046317	0.624788	0.463732	0.036*
C7	0.1580 (3)	0.4837 (5)	0.5352 (3)	0.0279 (10)
H7	0.139987	0.441860	0.594392	0.034*
C8	0.2431 (3)	0.4540 (5)	0.5036 (3)	0.0227 (9)
C9	0.2417 (3)	0.5418 (5)	0.4113 (3)	0.0264 (9)
H9	0.289314	0.545450	0.373403	0.032*
C10	0.1577 (3)	0.6215 (5)	0.3865 (4)	0.0324 (11)
H10	0.138905	0.687842	0.328685	0.039*
C11	0.3238 (3)	0.3695 (5)	0.5673 (3)	0.0242 (9)
C12	0.3902 (3)	0.3077 (5)	0.5121 (3)	0.0232 (9)
C13	0.3666 (3)	0.2609 (5)	0.4068 (3)	0.0274 (10)
H13	0.307077	0.273153	0.356037	0.033*
C14	0.5156 (3)	0.2001 (5)	0.4781 (3)	0.0280 (10)
H14	0.576816	0.162377	0.484632	0.034*
C15	0.4868 (3)	0.2692 (5)	0.5584 (3)	0.0231 (9)
C16	0.5523 (3)	0.3104 (5)	0.6626 (3)	0.0224 (9)
C17	0.5507 (3)	0.4485 (5)	0.7038 (3)	0.0262 (9)
H17	0.502167	0.512696	0.669080	0.031*
C18	0.6193 (3)	0.4925 (5)	0.7946 (3)	0.0289 (10)
H18	0.617676	0.586067	0.822470	0.035*
C19	0.6896 (3)	0.3990 (5)	0.8438 (4)	0.0325 (11)
C20	0.6919 (3)	0.2610 (5)	0.8077 (4)	0.0324 (11)
H20	0.740068	0.197122	0.843962	0.039*
C21	0.6222 (3)	0.2166 (5)	0.7170 (4)	0.0300 (10)
H21	0.622439	0.121277	0.691958	0.036*

3 Comment

Ferrocene, known for its robust and well-defined sandwich structure, serves as an ideal scaffold for incorporating diverse functional moieties,[4] The single-crystal structure of (4-(4-chlorophenyl)-1*H*-pyrrole-3-carbonyl)ferrocene, with the incorporation of a pyrrole-3-carbonyl group, along with a 4-chlorophenyl substituent, introduces additional versatility to the molecule, potentially enhancing its applications in fields.[5–10]

In the crystal of the title compound, the iron center of ferrocene is coordinated to two cyclopentadienyl rings, which adopt a parallel alignment, a characteristic feature of the ferrocene structure.[11–14] The functionalized pyrrole-3-carbonyl group is attached to the ferrocene scaffold through the carbonyl carbon atom (C11), which interacts with the C12 atom and connects the two ring systems. The bond length of C11–C8 is 1.480(6) Å, and the bond length of C11–C12 is 1.465(7) Å. The 4-chlorophenyl group, represented by atoms C16 to C21 in the structure, is positioned at the para position relative to the pyrrole ring, as indicated by the spatial arrangement in the crystal. The chlorine atom (Cl1) is attached to carbon atom C19, and the bond length of Cl1–C19 is 1.745(5) Å.

The dihedral angle between the two cyclopentadienyl rings is measured to be 5.2°, reflecting a nearly parallel alignment, which is in agreement with the structural features observed in other ferrocenyl compounds.[15–18] Furthermore, the dihedral angle between the chlorophenyl and pyrrole rings is determined to be 42.3°, which is slightly smaller than the 51° angle reported for the analogous compound 4-(2-chlorophenyl)-1*H*-pyrrol-3-yl (ferrocenyl) methanone.[19]

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