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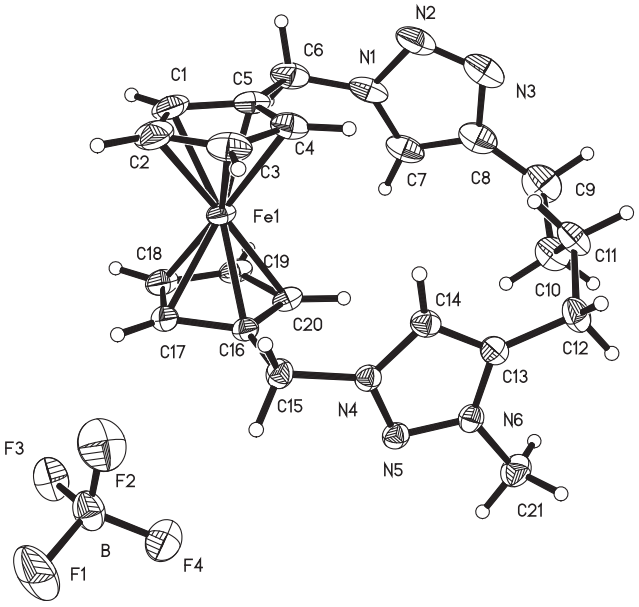
Crystal structure of 3-methyl-cyclobis(1-(1,1′-ferrocenylmethyl)-4-butyl-1*H*-1,2,3-triazole) tetrafluoroborate, $C_{21}H_{25}FeN_6 \cdot BF_4$



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Abstract

$C_{21}H_{25}FeN_6 \cdot BF_4$, monoclinic, *Pn* (no. 7), $a = 9.6166(5)$ Å, $b = 10.8331(6)$ Å, $c = 11.0982(6)$ Å, $\beta = 105.997(2)°$, $V = 1111.41(10)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0388$, $wR_{ref}(F^2) = 0.0831$, $T = 180(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	$0.25 \times 0.20 \times 0.15$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.73 mm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
θ_{max}, completeness:	29.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	21103, 5944, 0.029
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5050
$N(param)_{refined}$:	299
Programs:	Bruker [1], SHELX [2, 3]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Fe1	0.89685(5)	0.70110(3)	0.09053(4)	0.03669(12)
C1	0.9248(5)	0.5289(4)	0.0280(5)	0.0603(12)
H1A	0.8569	0.4854	−0.0440	0.072*
C2	1.0403(5)	0.6064(4)	0.0208(5)	0.0678(13)
H2A	1.0679	0.6274	−0.0573	0.081*
C3	1.1100(4)	0.6490(4)	0.1423(5)	0.0593(11)
H3A	1.1953	0.7058	0.1655	0.071*
C4	1.0372(4)	0.5985(3)	0.2253(4)	0.0498(9)
H4A	1.0620	0.6131	0.3177	0.060*
C5	0.9210(4)	0.5241(3)	0.1540(4)	0.0478(9)
C6	0.8193(5)	0.4494(3)	0.2063(4)	0.0607(11)
H6A	0.7190	0.4626	0.1538	0.073*
H6B	0.8423	0.3607	0.2020	0.073*
C7	0.7563(4)	0.5667(4)	0.3803(4)	0.0546(10)
H7A	0.6774	0.6157	0.3347	0.066*
C8	0.8195(5)	0.5692(4)	0.5064(5)	0.0594(11)
C9	0.7828(5)	0.6437(5)	0.6049(5)	0.0738(14)
H9A	0.8252	0.6040	0.6872	0.089*
H9B	0.6764	0.6444	0.5897	0.089*
C10	0.8370(5)	0.7777(4)	0.6107(5)	0.0588(10)
H10A	0.7964	0.8167	0.5278	0.071*
H10B	0.7999	0.8238	0.6725	0.071*
C11	0.9996(4)	0.7893(4)	0.6463(4)	0.0532(10)
H11A	1.0379	0.7353	0.5910	0.064*
H11B	1.0396	0.7600	0.7335	0.064*
C12	1.0513(4)	0.9214(4)	0.6363(3)	0.0495(9)
H12A	1.0055	0.9772	0.6849	0.059*
H12B	1.1573	0.9254	0.6734	0.059*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C13	1.0154(3)	0.9643(3)	0.5042(3)	0.0368(7)
C14	1.0649(4)	0.9255(3)	0.4062(3)	0.0382(7)
H14A	1.1347	0.8630	0.4082	0.046*
C15	0.9945(4)	0.9791(3)	0.1758(3)	0.0390(7)
H15A	1.0906	0.9504	0.1711	0.047*
H15B	0.9742	1.0596	0.1324	0.047*
C16	0.8805(4)	0.8868(3)	0.1129(3)	0.0339(7)
C17	0.8412(4)	0.8555(3)	−0.0167(3)	0.0446(8)
H17A	0.8889	0.8863	−0.0804	0.054*
C18	0.7226(4)	0.7722(3)	−0.0393(4)	0.0520(10)
H18A	0.6727	0.7338	−0.1218	0.062*
C19	0.6883(4)	0.7513(3)	0.0751(4)	0.0454(8)
H19A	0.6101	0.6961	0.0874	0.054*
C20	0.7850(4)	0.8230(3)	0.1694(3)	0.0385(7)
H20A	0.7870	0.8264	0.2599	0.046*
C21	0.8294(4)	1.1311(4)	0.5123(4)	0.0527(9)
H21A	0.8484	1.1084	0.6008	0.079*
H21B	0.8539	1.2182	0.5058	0.079*
H21C	0.7267	1.1182	0.4696	0.079*
N1	0.8278(4)	0.4811(3)	0.3335(4)	0.0558(9)
N2	0.9331(4)	0.4305(4)	0.4256(4)	0.0716(11)
N3	0.9277(4)	0.4840(4)	0.5308(4)	0.0747(11)
N4	0.9953(3)	0.9934(2)	0.3071(2)	0.0336(5)
N5	0.9054(3)	1.0727(2)	0.3338(3)	0.0356(6)
N6	0.9177(3)	1.0541(2)	0.4533(2)	0.0349(6)
B	0.9441(5)	1.1621(5)	−0.1242(4)	0.0562(11)
F1	0.9873(4)	1.2513(4)	−0.1925(3)	0.1112(13)
F2	1.0535(3)	1.0789(3)	−0.0771(3)	0.0949(10)
F3	0.8306(2)	1.0980(3)	−0.2037(2)	0.0661(7)
F4	0.8963(5)	1.2093(3)	−0.0284(3)	0.0970(11)

Source of material

Firstly, the neutral bitriazole cycle was prepared by clicking reaction of 1,1′-bis(azidomethyl)ferrocene and 1,7-octanediyne *via* the literature method [4]. Then, 0.5 mmol of this neutral precursor and 1 mmol of $(MeO)_3BF_4$ were added into 30 mL dichloromethane solution. The mixture was reacted for 24 h at room temperature, and 1 mL of methanol was added to quench the reaction. The mixture was evaporated to dryness under reduced pressure. The crude mixture was purified by crystallisation using a dichloromethane/hexane mixture as the solvent. Yellow single crystals were obtained by slow vapor diffusion of ethyl ether into a dichloromethane solution.

Experimental details

Hydrogen atoms were placed in their geometrically idealised positions and constrained to ride on their parent atoms.

Comment

The Cu(I)-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC) reaction [5], one of the most widely used "click reactions", has been wildly used to synthesise novel chemosensor [6, 7]. The click derived 1,2,3-triazole ring is a good donor for both metal ions and anions *via* metal-N coordination or CH$\cdots$anions hydrogen bonding. Herein, we synthesise a new ferrocence-containing macrocycle using the aforementioned click reaction, and report its crystal structure.

The asymmetric unit of the title crystal structure contains the cyclic cation and the tetrafluoroborate anion. The cyclic ligand exhibits a cavity with the N1—N4 distance of 5.8 Å, and the Fe1—C10 distance of 6.0 Å, respectively. The dihedral angle between the planes defined by the triazole rings is 21.10(15) Å. In the ferrocene part, the iron atom is sandwiched almost perfectly centrally between the two cyclopentadienyl rings, with the Fe—C bond lengths in the range 2.012(7)–2.040(8) Å within the normal range [8]. The two cyclopentadienyl rings are not eclipsed, with the torsion angle of 13.7°.

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