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Crystal structure of 4-(5,5-difluoro-1,3,7,9-tetramethyl-3*H*,5*H*-5 λ^4 -dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-10-yl)pyridin-1-ium tetraiodidoferrate(III), C₁₈H₁₉BF₂FeI₄N₃

Table 1: Data collection and handling.

Crystal:	Black needle
Size:	0.60 × 0.10 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	5.43 mm ⁻¹
Diffractometer, scan mode:	Gemini, ω
$\theta_{\max}$, completeness:	25.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	9106, 4499, 0.024
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3386
$N(\text{param})_{\text{refined}}$:	270
Programs:	SHELX [1], Olex2 [2], CrysAlis ^{PRO} [3]

<https://doi.org/10.1515/ncrs-2019-0226>

Received March 26, 2019; accepted May 6, 2019; available online May 22, 2019

Abstract

C₁₈H₁₉BF₂FeI₄N₃, triclinic, $P\bar{1}$ (no. 2), $a = 8.2997(3)$ Å, $b = 11.8180(9)$ Å, $c = 14.0849(7)$ Å, $\alpha = 106.388(5)^\circ$, $\beta = 101.841(4)^\circ$, $\gamma = 95.200(4)^\circ$, $V = 1280.88(13)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0393$, $wR_{\text{ref}}(F^2) = 0.1045$, $T = 293(2)$ K.

CCDC no.: 1914112

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was synthesized by a reaction between a BODIPY-modified pyridine ligand and [Fe(CO)₄I₂] to afford a black solid. The BODIPY derivative and [Fe(CO)₄I₂] were prepared according to reference methods [4–6]. Single crystals suitable for X-ray diffraction analysis were obtained by a solvent diffusion method between dichloromethane and *n*-hexane solvents.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
B1	0.7571(7)	0.8695(6)	0.4627(5)	0.0396(16)
C1	1.3558(7)	0.7387(7)	0.2215(5)	0.0538(18)
H1	1.462061	0.77744	0.228178	0.065*
C2	1.2606(6)	0.7921(6)	0.2808(4)	0.0499(17)
H2	1.297728	0.868604	0.326352	0.060*
C3	1.1037(6)	0.7305(5)	0.2731(4)	0.0365(14)
C4	1.0535(7)	0.6191(5)	0.2034(4)	0.0433(15)
H4	0.949190	0.577008	0.196346	0.052*
C5	1.1547(7)	0.5697(6)	0.1444(5)	0.0522(17)
H5	1.121589	0.493227	0.098367	0.063*
C6	0.9948(6)	0.7831(5)	0.3403(4)	0.0350(14)
C7	0.9886(6)	0.7421(5)	0.4221(4)	0.0374(14)
C8	1.0810(7)	0.6654(6)	0.4652(5)	0.0488(16)
C9	1.0224(8)	0.6621(6)	0.5499(5)	0.0529(16)
H9	1.059384	0.618758	0.593650	0.064*
C10	0.8992(7)	0.7342(6)	0.5589(5)	0.0522(17)
C11	0.7338(6)	1.0013(6)	0.3465(5)	0.0451(15)
C12	0.7965(7)	1.0120(6)	0.2639(5)	0.0522(17)
H12	0.769984	1.065542	0.227998	0.063*
C13	0.9014(6)	0.9322(6)	0.2445(4)	0.0427(15)
C14	0.9053(6)	0.8689(5)	0.3173(4)	0.0383(14)
C15	0.9962(8)	0.9204(7)	0.1632(5)	0.0595(18)
H15A	1.109518	0.958696	0.193679	0.089*
H15B	0.945476	0.957505	0.114695	0.089*
H15C	0.994217	0.837309	0.129231	0.089*
C16	0.6166(7)	1.0729(6)	0.3938(5)	0.0603(19)
H16A	0.678565	1.142606	0.446962	0.090*
H16B	0.551404	1.025633	0.422013	0.090*
H16C	0.544088	1.096643	0.342932	0.090*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C17	1.2159(8)	0.6012(7)	0.4325(5)	0.0618(19)
H17A	1.172004	0.542945	0.366759	0.093*
H17B	1.259342	0.561955	0.481120	0.093*
H17C	1.303645	0.657329	0.428671	0.093*
C18	0.7991(9)	0.7537(7)	0.6369(6)	0.068(2)
H18A	0.695857	0.699172	0.610415	0.102*
H18B	0.776357	0.834284	0.653244	0.102*
H18C	0.860397	0.740298	0.697326	0.102*
F1	0.5931(3)	0.8072(3)	0.4314(3)	0.0566(10)
F2	0.7693(4)	0.9616(3)	0.5516(2)	0.0535(10)
Fe1	0.45894(11)	0.70675(9)	0.88590(7)	0.0535(3)
I1	0.64632(5)	0.65648(4)	1.03425(3)	0.05332(16)
I2	0.41353(7)	0.53462(6)	0.72273(4)	0.0864(2)
I3	0.61169(7)	0.89636(6)	0.88061(5)	0.0865(2)
I4	0.17419(5)	0.73544(5)	0.92156(4)	0.07148(19)
N1	1.3017(6)	0.6316(6)	0.1531(4)	0.0545(16)
H19	1.349(8)	0.587(6)	0.111(5)	0.07(2)*
N2	0.8783(5)	0.7835(4)	0.4831(3)	0.0406(12)
N3	0.7982(5)	0.9163(4)	0.3787(3)	0.0388(12)

Experimental details

Crystallographic data of title compound were collected on a Gemini diffractometer with graphite-monochromated Mo-K α radiation using ω -scans. Structure was determined using direct methods in SHELXS program and refined by full-matrix least-squares routines. All the non-hydrogen atoms were anisotropically refined, and hydrogen atoms were located by geometrical calculation.

Comment

Boron dipyrromethenes (BODIPY) have received increasing attention as high-performance fluorescent dyes in the past decades due to their unique optical properties and convenient chemical modification. Therefore, BODIPYs have wide applications in series of fields as sensors, photosensitizers, fluorescence labeling agents, anticancer drugs, and so on [7].

Herein, a new ionic BODIPY-based fluorescent dye containing a pyridinium group is reported, which was prepared by the reaction of a BODIPY-modified pyridine ligand and Hieber reagent [Fe(CO)₄I₂] at humid condition. The Hieber reagent decomposed in the THF solvent with CO release at the aid of a nucleophilic substitution of pyridine

group. Tetraiodoferrate (III) salts were finally produced with the organic pyridine group protonated. Additionally, the title compound carried on high-performance luminescence accompanying with suitable water-solubility, which should be attributed to its ionicity. These features present it as a promising imaging reagent in biological and medical fields. Geometric parameters are in the expected ranges [8, 9].

Acknowledgements: This work was supported by the Zhejiang Provincial Natural Science Foundation of China (No. LQ17B010004), Zhejiang Provincial Science and Technology Innovation Project for College Students (No. 2018R417030), and Jiaxing University Key SRT Project (No. 85178557).

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