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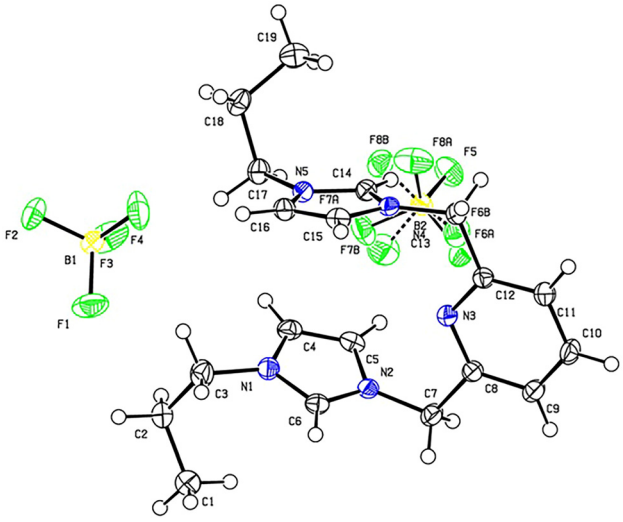
Crystal structure of 3,3′-(pyridine-2,6-diylbis(methylene))bis(1-propyl-1*H*-imidazol-3-ium) ditetrafluoroborate, $C_{19}H_{27}B_2F_8N_5$



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Abstract

$C_{19}H_{27}N_5$, orthorhombic *Pbca* (no. 61), a = 9.8515(12) Å, b = 16.508(2) Å, c = 29.817(3) Å, β = 90°, V = 4849.3(10) Å^3, Z = 8, $R_{gt}(F)$ = 0.0409, $wR_{ref}(F^2)$ = 0.1082.

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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.

Table 1: Data collection and handling.

Crystal:	Colorless plate
Size:	0.27 × 0.22 × 0.14 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.13 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	31,833, 5336, 0.029
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 4368
$N(param)_{refined}$:	337
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4], WinGX/ORTEP [5]

Source of material

The title compound was prepared using a method described in the literature [6]. In a 50 mL round-bottom flask, *N*-propyl imidazole (1.0 mmol) and 2,6-bis(chloromethyl)pyridine (0.5 mmol) were gently stirred together under inert conditions. The temperature was gradually raised, and the neat molten mixture maintained at 60 °C for 16 h. The light brown crude solid that resulted was allowed to cool to room temperature before being loaded onto a short plug of silica gel. The unreacted starting materials were washed with EtOAc, and the product salt bearing dichloride counterions was obtained as an eluent of MeOH (100%). Removal of all volatiles under reduced pressure gave the bisimidazolium dichloride salt as clear viscous oil in excellent yield. Successively, anionic metathesis of the chloride salt was achieved by dropwise addition of saturated aqueous solution of $NaBF_4$ (2.5 mol equiv.) to its methanolic solution. The resultant mixture was then stirred at room temperature for 20 h. At the end of the reaction time, the contents in the reaction flask were concentrated under vacuum and organics extracted with acetone (3 × 20 mL). Subsequent solvent removal afforded the title compound as a brown solid: yield 0.25 g (90%). Colorless single crystals suitable for X-ray analysis were obtained by layering the methanolic solution of the title compound with diethyl ether [7, 8]. **^{1}H NMR** (CD_3CN, 400 MHz) δ/ppm: 0.90 (t, J = 7.4 Hz, 2 × 3H,

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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}
B1	0.74157 (17)	0.90551 (10)	0.74844 (6)	0.0234 (3)
B2	0.14461 (17)	0.69821 (10)	0.55973 (5)	0.0217 (3)
C1	0.4246 (2)	0.60186 (11)	0.81026 (6)	0.0438 (5)
H1A	0.376509	0.570499	0.787324	0.066*
H1B	0.370936	0.602651	0.837924	0.066*
H1C	0.513040	0.576852	0.816193	0.066*
C2	0.44571 (19)	0.68936 (10)	0.79347 (5)	0.0325 (4)
H2A	0.356204	0.713743	0.786725	0.039*
H2B	0.488354	0.721732	0.817608	0.039*
C3	0.53546 (18)	0.69356 (11)	0.75121 (6)	0.0339 (4)
H3A	0.626555	0.671674	0.758273	0.041*
H3B	0.546437	0.750852	0.742108	0.041*
C4	0.36837 (15)	0.67242 (9)	0.68566 (5)	0.0245 (3)
H4	0.324407	0.723604	0.686676	0.029*
C5	0.33921 (15)	0.60988 (9)	0.65713 (5)	0.0242 (3)
H5	0.272049	0.609724	0.634269	0.029*
C6	0.50776 (14)	0.56966 (9)	0.70181 (5)	0.0221 (3)
H6	0.576152	0.537467	0.715481	0.026*
C7	0.43525 (17)	0.46741 (9)	0.64459 (5)	0.0274 (3)
H7A	0.342503	0.448128	0.637558	0.033*
H7B	0.478197	0.427248	0.664749	0.033*
C8	0.51809 (15)	0.47322 (9)	0.60082 (5)	0.0212 (3)
C9	0.53983 (16)	0.40225 (9)	0.57566 (5)	0.0248 (3)
H9	0.502033	0.352030	0.584934	0.030*
C10	0.61881 (16)	0.40739 (9)	0.53645 (5)	0.0273 (3)
H10	0.636432	0.360443	0.518974	0.033*
C11	0.67140 (16)	0.48328 (9)	0.52351 (5)	0.0255 (3)
H11	0.725178	0.488521	0.497227	0.031*
C12	0.64225 (15)	0.55131 (9)	0.55054 (5)	0.0210 (3)
C13	0.69277 (16)	0.63536 (9)	0.53542 (5)	0.0246 (3)
H13A	0.644771	0.650911	0.507543	0.029*
H13B	0.790854	0.631921	0.528453	0.029*
C14	0.55351 (15)	0.73926 (9)	0.57695 (5)	0.0215 (3)
H14	0.472407	0.733089	0.560052	0.026*
C15	0.76584 (15)	0.72439 (9)	0.60168 (5)	0.0239 (3)
H15	0.856555	0.705588	0.604567	0.029*
C16	0.70346 (15)	0.78112 (9)	0.62814 (5)	0.0241 (3)
H16	0.742930	0.809464	0.652609	0.029*
C17	0.47043 (16)	0.85037 (10)	0.62913 (5)	0.0274 (3)
H17A	0.477677	0.854389	0.662170	0.033*
H17B	0.377324	0.832184	0.621726	0.033*
C18	0.49573 (18)	0.93455 (10)	0.60811 (6)	0.0307 (4)
H18A	0.434786	0.974469	0.622543	0.037*
H18B	0.590411	0.951156	0.614378	0.037*
C19	0.4719 (2)	0.93634 (11)	0.55697 (6)	0.0403 (4)
H19A	0.537253	0.900436	0.542170	0.060*
H19B	0.483904	0.991756	0.545865	0.060*
H19C	0.379434	0.917971	0.550384	0.060*
F1	0.77417 (12)	0.84260 (6)	0.77795 (4)	0.0493 (3)
F2	0.77939 (10)	0.98057 (6)	0.76741 (3)	0.0358 (2)
F3	0.60173 (10)	0.90432 (7)	0.74013 (5)	0.0522 (3)
F4	0.81231 (12)	0.89578 (7)	0.70765 (3)	0.0501 (3)
F5	0.03182 (10)	0.71304 (6)	0.53157 (3)	0.0353 (2)
F6A[a]	0.1795 (2)	0.61542 (8)	0.55926 (5)	0.0403 (4)
F6B[b]	0.2349 (12)	0.6372 (7)	0.5512 (3)	0.0344 (19)
F7A[a]	0.11646 (18)	0.72291 (12)	0.60368 (4)	0.0418 (4)
F7B[b]	0.0872 (12)	0.6873 (9)	0.6023 (3)	0.045 (3)
F8A[a]	0.25513 (13)	0.74281 (11)	0.54236 (6)	0.0448 (5)
F8B[b]	0.2284 (10)	0.7690 (5)	0.5625 (4)	0.0337 (18)
N1	0.47551 (13)	0.64657 (8)	0.71311 (4)	0.0232 (3)
N2	0.42655 (12)	0.54648 (7)	0.66793 (4)	0.0207 (3)
N3	0.56774 (12)	0.54712 (7)	0.58879 (4)	0.0214 (3)
N4	0.67120 (12)	0.69936 (7)	0.56968 (4)	0.0201 (3)
N5	0.57062 (12)	0.78936 (7)	0.61226 (4)	0.0205 (3)

[a]Occupancy: 0.882 (4), [b]Occupancy: 0.118 (4).

CH_3); 1.87 (m, 2 × 2H, CH_2); 4.26 (t, J = 7.2 Hz, 2 × 2H, CH_2); 5.54 (s, 2 × 2H, $CH_{2(lutidyl)}$); 7.46 (d, J = 1.5 Hz, 2 × 1H, $CH_{lutidyl}$) 7.53 (d, J = 7.7 Hz, 2 × 1H, −CH=$_{imidazolyl}$), 7.60 (t, J = 1.6 Hz, 2 × 1H, =CH−$_{imidazolyl}$), 7.87 (t, J = 7.7 Hz, 1H, $CH_{lutidyl}$); 9.83 (s, 2 × 1H, NC*H*N$_{imidazolyl}$). **^{13}C NMR** (CD_3CN, 100.6 MHz) δ/ppm: 10.84 (CH_3), 24.22 (CH_2), 51.92(CH_2), 54.19 ($CH_{2(lutidyl)}$), 122.92, 123; 89, 124.10, 139.91, 154.57 (NCHN). **HRMS-ES$^+$:** (m/z)/2: calcd for [(M − 2BF_4)]/2 162.6128, found 162.6140.

Experimental details

Crystal evaluation was carried out using a Bruker APEX-II diffractometer [1] outfitted with an Oxford Cryostream low-temperature apparatus set to 104 K. The structure was solved with the ShelXT [3] structure solution program using Intrinsic Phasing and refined with the ShelXL [4] refinement package. U_{iso} was fixed at 1.2 times of C(H) and C(H, H) groups and at 1.5 times of C(H, H, H) group and secondary CH_2 and aromatic H were refined with riding coordinates. Methyl was idealized and refined as a rotating group. The visual crystal structure information was performed using ORTEP-3 [5].

Comment

When adequately constituted, the title compound can be a convenient source of ionic liquid (IL) solvents [7, 8]; it is also a credible alternative to phosphines in organometallic chemistry and catalysis [9]. More importantly, when combined with metal ions, the complexes have been used as catalysts in various applications [10–12].

The title structure is composed of one cationic pyridine bridged bis-imidazole core and two tetrafluoroborate anions occupying the asymmetric unit. Both imidazole units in the title structure are almost perpendicular to the plane

of the central pyridine unit, and the imidazole C-2 protons are directed well away from each other. The internal ring angle of imidazole (N–C–N) is 108.35(13) for N1–C6–N2 and 108.47(12) for N4–C14–N5, which are well within the range for related imidazole-based salts [13, 14]. A series of weak C–H···F hydrogen bonding interactions between the counterions and the core salt, which were observed in the extended structure of the compound, stabilized the crystal packing.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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