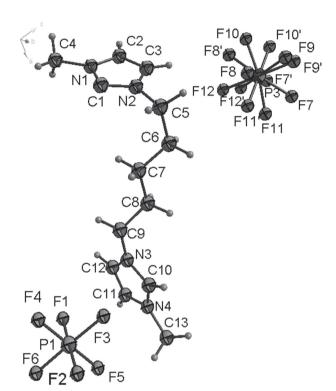
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Crystal structure of 1,1'-(pentane-1,5-diyl)bis(3-methyl-1H-imidazol-3-ium)bis(hexafluoro-phosphate), $C_{13}H_{22}F_{12}N_4P_2$



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Abstract

 $C_{13}H_{22}F_{12}N_4P_2$, monoclinic, $P2_1/c$, a = 12.9171(13) Å, b = 13.3953(13) Å, c = 12.5808(12) Å, $\beta = 97.766(1)^\circ$,

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 $V = 2156.9(4) \text{ Å}^3$, Z = 4, $R_{\rm gt}(F) = 0.0583$, $wR_{\rm ref}(F^2) = 0.1557$, T = 296(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.

Table 1: Data collection and handling.

Crystal:Colorless blockSize: $0.21 \times 0.20 \times 0.19 \text{ mm}$ Wavelength:Mo $K\alpha$ radiation (0.71073 Å)

 μ : 0.31 mm⁻¹

Diffractometer, scan mode: Bruker APEX-II, φ and ω -scans

 $\theta_{\rm max}$, completeness: 25.5°, >99% $N(hkl)_{\rm measured}$, $N(hkl)_{\rm unique}$, $R_{\rm int}$: 16239, 4010, 0.033 Criterion for $I_{\rm obs}$, $N(hkl)_{\rm gt}$: $I_{\rm obs} > 2 \, \sigma(I_{\rm obs})$, 2890

 $N(param)_{refined}$: 338

Programs: Bruker programs [1], SHELX [2]

Source of materials

1-Methylimidazole (8.21 g, 0.1 mol) was dissolved in methylbenzene (20 mL), 1,5-dibromopentane (11.35 g, 0.05 mol) was quickly added under stirring. The mixture first reacted at 90 °C for 10 min, and then heated to 110 °C for 7-10 hours. After the reaction has completed (monitored by TLC), a white solid was produced. The resulting suspension was filtered, crushed and washed with hexane, ethylacetate and diethyl ether three times respectively. Then the intermediate (C5M-Br)(0.5 g, 0.00127 mol), potassium hexafluorophosphate (0.6 g, 0.0029 mol) was dissolved in deionized water (20 mL). The mixture stirred well for 12 h at 85 °C and then cooled slowly. Colorless crystals were produced and filtered. They were washed with deionized water many times until silver bromide precipitation occurs anymore. The product (0.1 g) was dissolved in ethanol: water (2:1) solution and (7 mL), then the mixture reacted in the microwave synthesizer at 100 °C for 2 min. Crystals suitable for X-ray analysis were obtained after cooled slowly.

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

Atom	х	у	Z	U _{iso} */U _{eq}
N1	-0.1664(2)	0.2727(2)	0.4032(2)	0.0650(7)
N2	-0.02379(19)	0.28810(19)	0.5099(2)	0.0575(7)
N3	0.3493(2)	0.4298(2)	0.2098(2)	0.0652(7)
N4	0.4863(2)	0.5092(2)	0.1792(2)	0.0686(8)
P1	0.52608(7)	0.20209(6)	0.07292(7)	0.0603(3)
Р3	0.07664(8)	0.51739(8)	0.81503(8)	0.0724(3)
F1	0.4346(2)	0.2733(2)	0.0285(3)	0.1443(12)
F2	0.61817(18)	0.13149(18)	0.1215(2)	0.0992(8)
F3	0.5080(2)	0.2244(2)	0.1927(2)	0.1141(9)
F4	0.44853(19)	0.11101(19)	0.0688(2)	0.1060(8)
F5	0.6052(2)	0.2914(2)	0.0786(2)	0.1276(11)
F6	0.5471(2)	0.1799(3)	-0.04392(19)	0.1306(11)
F7 ^a	0.1675(11)	0.5845(8)	0.8689(11)	0.190(5)
F8 ^a	0.0986(13)	0.4094(5)	0.8066(12)	0.189(5)
F9 a	0.1122(9)	0.4474(10)	0.9202(10)	0.152(4)
F10 ^a	-0.0404(5)	0.4992(14)	0.8311(12)	0.173(6)
F11 ^a	0.1830(7)	0.5365(10)	0.7795(16)	0.179(6)
F12 ^a	0.0365(11)	0.5282(6)	0.6908(5)	0.134(4)
F7'b	0.0548(10)	0.6326(6)	0.8133(8)	0.132(4)
F8' ^b	0.0027(13)	0.4322(12)	0.7749(6)	0.165(6)
F9'b	0.1056(12)	0.5216(16)	0.9296(7)	0.192(6)
F10'b	-0.0001(12)	0.5584(13)	0.8789(12)	0.200(6)
F11' ^b	0.1527(12)	0.476(2)	0.7517(12)	0.272(11)
F12'b	0.0396(11)	0.590(3)	0.733(3)	0.337(14)
C1	-0.0707(3)	0.2384(2)	0.4278(3)	0.0645(8)
H1	-0.041181	0.186915	0.392340	0.077*
C2	-0.1801(3)	0.3470(3)	0.4727(3)	0.0782(10)
H2	-0.240510	0.384554	0.473694	0.094*
C3	-0.0921(3)	0.3568(3)	0.5389(3)	0.0747(10)
H3	-0.079358	0.402278	0.595040	0.090*
C4	-0.2423(3)	0.2406(4)	0.3117(3)	0.0999(14)
H4A	-0.248121	0.291045	0.257087	0.150*
H4B	-0.309208	0.230400	0.335190	0.150*
H4C	-0.219075	0.179265	0.283233	0.150*
C5	0.0838(3)	0.2752(3)	0.5611(3)	0.0737(10)
H5A	0.105875	0.207134	0.550145	0.088*
H5B	0.086822	0.285836	0.637739	0.088*
C6	0.1583(3)	0.3466(3)	0.5171(3)	0.0739(10)
H6A	0.129306	0.413406	0.516620	0.089*
H6B	0.223874	0.347000	0.564912	0.089*
C7	0.1801(3)	0.3216(3)	0.4062(3)	0.0704(9)
H7A	0.114245	0.317584	0.359115	0.085*
H7B	0.212818	0.256411	0.407454	0.085*
C8	0.2501(3)	0.3968(3)	0.3602(3)	0.0650(8)
H8A	0.213024	0.459562	0.347692	0.078*
H8B	0.311672	0.408674	0.411869	0.078*
C9	0.2822(4)	0.3611(3)	0.2589(4)	0.0971(14)
H9A	0.318817	0.298191	0.272298	0.117*
H9B	0.220072	0.348424	0.208327	0.117*
C10	0.4486(3)	0.4454(2)	0.2431(3)	0.0641(8)
H10	0.486480	0.415782	0.302964	0.077*
C11	0.4081(4)	0.5357(3)	0.1021(3)	0.0852(12)
H11	0.412862	0.580438	0.046474	0.102*

Table 2 (continued)

Atom	х	у	Z	U _{iso} */U _{eq}
H12	0.257583	0.489575	0.078931	0.102*
C13	0.5941(4)	0.5428(4)	0.1882(4)	0.1133(17)
H13A	0.632832	0.499230	0.147563	0.170*
H13B	0.624474	0.541794	0.262166	0.170*
H13C	0.596154	0.609555	0.160811	0.170*

^aOccupancies: a = 526(7), b = 0.474(7).

Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with C-H = 0.93-0.97 Å with $U_{\rm iso}({\rm H}) = 1.5~U_{\rm eq}({\rm C})$ for methyl H atoms and 1.2 $U_{\rm eq}({\rm C})$ for all other H atoms. There is a disorder of one of the two hexafluorophosphate anions (cf. the figure).

Discussion

Ionic liquid, as a new type of environmentally friendly solvent and liquid acid base catalyst, owing to the advantages of adjustable structure, high catalytic efficiency, mild conditions, and can be recycled, etc, has been widely used in catalytic science, electrochemistry, environmental science, extraction and separation, biomass energy, resource conversion and other fields [3–5]. Because of the unique physical and chemical properties of ionic liquids, ionic liquids have the unique potential advantages of biodiesel preparation. In recent years, various functional ionic liquids have been synthesised, and have been used to prepare biodiesel highly efficiently and environmental friendly [6, 7]. It was found that dinuclear alkaline ionic liquid bis-(3-methyl-1-imidazolium-)ethlyene dihydroxide([MC2]OH) shows excellent catalytic efficiency, the highest conversion rate of cotton seed oil was up to 98.5%, and the stability of and separation effect of the catalyst was very ideal [8].

Recently, our group still focused on the preparation of biodiesel catalyzed by ionic liquid [9, 10] and reported two crystal structures of 1,1'-butanebis(3methyl-1*H*-imidazol-3-ium),bis(hexafluorophosphate) 1,1'-(hexane-1,6-diyl)bis(3-methyl-1*H*-imidazol-3-ium),

bis(hexafluorophosphate) [11, 12]. In order to find the ionic liquid catalyst with better catalytic efficiency, we were engaged in synthesising the novel ionic liquid catalyst with imidazole. Herein, we report the synthesis and structure of the bisimidazoles ionic liquid. Bond lengths and angles within the imidazole ring are very similar to those given in the literature for diimidazole ionic liquid [13]. The title structure consists of one C_5M^{2+} cation(1,1'-(pentane-1,5-diyl)bis(3methyl-1H-imidazol-3-ium)), and two PF $_6^-$ anions (cf. the figure). Two cationic 1-ethylimidazolium rings were bound

to the both sides of pentyl group. The two imidazole rings are almost crystallographically dependent planar and the dihedral angle of two imidazole rings is 89.207°.

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