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Crystal structure of 1,1'-methylenebis(3-ethyl-1*H*-imidazol-3-ium) bis(hexafluorophosphate(V)), $C_{11}H_{18}F_{12}N_4P_2$

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.20 × 0.12 × 0.12 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.34 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
$\theta_{\max}$, completeness:	25.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	14106, 3570, 0.043
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2259
$N(\text{param})_{\text{refined}}$:	304
Programs:	Bruker programs [1], SHELX [2]

Source of materials

1-Ethylimidazole (9.61 g, 0.1 mol) was dissolved in methylbenzene (20 mL), 1,2-dibromomethane (8.70 g, 0.05 mol) was quickly added under stirring. The mixture first reacted at 60 °C for 10 min, and then heated to 110 °C for 8 h. After the reaction completed (monitored by TLC), a white solid was produced after cooled slowly. The resulting suspension was filtered, crushed and washed with ethyl acetate and diethyl ether 3 times respectively. The white powder intermediates (C1EM–Br) dried *in vacuo* (15.56 g, yield 85%). Then the intermediates (C1EM–Br) (1.10 g, 0.003 mol), potassium hexafluorophosphate (1.10 g, 0.006 mol) was dissolved in water (20 mL). The mixture stirred well for 12 h at 85 °C and then cooled slowly. Then crystals suitable for X-ray analysis were obtained.

Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with C–H = 0.90–0.97 Å with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ for methyl H atoms and 1.2 $U_{\text{eq}}(\text{C})$ for all other H atoms. One of the two hexafluorophosphate anions shows a disorder (*cf.* the figure; Table 2)

Comment

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

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Abstract

$C_{11}H_{18}F_{12}N_4P_2$, monoclinic, $P2_1/c$ (no. 14), $a = 14.975(3)$ Å, $b = 9.897(2)$ Å, $c = 13.525(3)$ Å, $\beta = 105.507(3)^\circ$, $V = 1931.5(7)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0590$, $wR_{\text{ref}}(F^2) = 0.1843$, $T = 296(2)$ K.

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The crystal 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.

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

Atom	x	y	z	U _{iso} ^a /U _{eq}
N1	0.64354(18)	0.8500(3)	0.8126(2)	0.0442(7)
N2	0.64395(17)	0.6342(3)	0.81526(19)	0.0394(6)
N3	0.74785(18)	0.4503(3)	0.8840(2)	0.0427(7)
N4	0.87592(19)	0.3683(3)	0.9774(2)	0.0518(8)
P1	0.85268(7)	0.76085(10)	0.64287(7)	0.0526(3)
P2	0.41790(7)	0.75019(8)	0.92372(7)	0.0456(3)
F1	0.94425(19)	0.6755(3)	0.6774(2)	0.1064(10)
F2	0.76110(15)	0.8502(2)	0.60531(17)	0.0731(7)
F3	0.86801(19)	0.7786(3)	0.53140(19)	0.0956(9)
F4	0.83498(18)	0.7465(2)	0.75284(17)	0.0730(7)
F5	0.91078(18)	0.8945(3)	0.6781(2)	0.0978(9)
F6	0.7923(2)	0.6315(3)	0.60493(19)	0.0911(8)
F7 ^a	0.3756(11)	0.6036(8)	0.9142(8)	0.093(5)
F8 ^b	0.5149(6)	0.679(2)	0.9702(8)	0.109(7)
F9 ^c	0.4634(16)	0.8877(10)	0.9366(10)	0.137(9)
F10 ^d	0.3219(9)	0.810(2)	0.8831(8)	0.131(8)
F11	0.4338(2)	0.7508(3)	0.81344(19)	0.0959(10)
F12	0.4025(2)	0.7486(2)	1.03569(18)	0.0793(8)
F7B ^e	0.4669(18)	0.6173(13)	0.9337(10)	0.153(10)
F8B ^f	0.5103(7)	0.823(2)	0.9716(8)	0.112(8)
F9B ^g	0.3686(14)	0.8930(12)	0.9073(8)	0.107(7)
F10B ^f	0.3234(10)	0.682(2)	0.8733(7)	0.131(11)
C1	0.6645(2)	0.7443(3)	0.8722(3)	0.0434(8)
H1	0.6896	0.7462	0.9429	0.052*
C2	0.6085(2)	0.8067(4)	0.7140(3)	0.0511(9)
H2	0.5885	0.8614	0.6564	0.061*
C3	0.6080(2)	0.6723(4)	0.7151(2)	0.0489(9)
H3	0.5873	0.6154	0.6589	0.059*
C4	0.6519(2)	0.4975(3)	0.8549(3)	0.0506(9)
H4A	0.6150	0.4375	0.8031	0.061*
H4B	0.6273	0.4939	0.9144	0.061*
C5	0.7932(2)	0.4091(3)	0.9783(3)	0.0497(9)
H5	0.7696	0.4094	1.0353	0.060*
C6	0.8055(3)	0.4347(4)	0.8225(3)	0.0573(10)
H6	0.7919	0.4556	0.7530	0.069*
C7	0.8845(3)	0.3840(4)	0.8796(3)	0.0618(10)
H7	0.9364	0.3629	0.8573	0.074*
C8	0.6570(3)	0.9904(4)	0.8483(4)	0.0737(12)
H8A	0.6472	0.9966	0.9162	0.088*
H8B	0.6114	1.0474	0.8026	0.088*
C9	0.7503(3)	1.0400(4)	0.8521(4)	0.0947(17)
H9A	0.7956	0.9853	0.8988	0.142*
H9B	0.7562	1.1321	0.8752	0.142*
H9C	0.7601	1.0349	0.7849	0.142*
C10	0.9460(3)	0.3124(4)	1.0663(3)	0.0715(12)
H10A	1.0071	0.3418	1.0635	0.086*
H10B	0.9351	0.3475	1.1290	0.086*
C11	0.9437(4)	0.1650(5)	1.0687(5)	0.128(3)
H11A	0.8889	0.1358	1.0866	0.192*
H11B	0.9976	0.1323	1.1188	0.192*
H11C	0.9432	0.1301	1.0023	0.192*

^aOccupancies: ^a = 0.54(2), ^b = 0.52(2), ^c = 0.51(2), ^d = 0.51(3),
^e = 0.46(2), ^f = 0.48(2), ^g = 0.49(2), ^h = 0.49(3).

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 synthesized, 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)-ethylene dihydroxide([MC₂]OH) shows excellent catalytic efficiency, the highest conversion rate of cotton seed oil was up to 98.5%, and the stability and separation effect of the catalyst was very ideal [8].

Recently, our group still focused on biodiesel catalysis in ionic liquids [9, 10] and reported four related crystal structures [11–14]. In order to find an ionic liquid catalyst with better catalytic efficiency, we were engaged in synthesizing the ionic liquid catalyst with imidazole.

Bond lengths and angles within the imidazole ring are very similar to those given in the literature for diimidazole ionic liquid [14]. The title structure consists of one C1EM²⁺ 1,1'-methylenebis(3-ethyl-1H-imidazol-3-ium) cation and two PF₆[−] anions (*cf.* the figure). Two cationic 1-ethylimidazolium rings were bound to the both sides of methylene group. The dihedral angle of two imidazole rings is 74.67(1)°. The torsion angles of C4–N2–C2–C3 and C4–N3–C6–C7 are 176.0(3)° and 177.3(4)°, respectively.

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References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2009).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Zhen, B.; Jiao, Q. Z.; Wu, Q.; Li, H. S.: Catalytic performance of acidic ionic liquid-functionalized silica in biodiesel production. *Energy. Chem. J.* **23** (2014) 97–104.
4. Rafiee, E.; Eavani, S.: A new organic–inorganic hybrid ionic liquid polyoxometalate for biodiesel production. *Mol. Liq. J.* **199** (2014) 96–101.
5. Fan, M. M.; Zhou, J. J.; Han, Q. J.; Zhang, P. B.: Effect of various functional groups on biodiesel synthesis from soybean oils by acidic ionic liquids. *Chin. Chem. Lett.* **23** (2012) 1107–1110.
6. Han, X. X.; He, Y. F.; Hung, C. T.; Liu, L. L.; Huang, S. J.; Liu, S. B.: Efficient and reusable polyoxometalate-based

- sulfonated ionic liquid catalysts for palmitic acid esterification to biodiesel. *Chem. Eng. Sci.* **104** (2013) 64–72.
7. Li, Y.; Hu, S. G.; Cheng, J. H.; Lou, W. Y.: Acidic ionic liquid catalyzed esterification of oleic acid for biodiesel synthesis. *Chin. J. Catal.* **35** (2014) 396–406.
 8. Liang, J. H.; Ren, X. Q.; Wang, J. T.: Preparation of biodiesel by transesterification from cottonseed oil using the basic dication ionic liquids as catalysts. *Wood. Chem. Technol. J.* **38** (2010) 275–280.
 9. Xiong, W. M.; Zhu, M. Z.; Deng, L.; Fu, Y.; Guo, Q. X.: Esterification of organic acid in bio-oil using acidic ionic liquid catalysts. *Energy Fuel.* **23** (2009) 2278–2283.
 10. Kong, J. H.; Lan, Y. D.; Chen, J.; Huang, C. G.; Xiong, W. M.: Preparation and component analysis of biodiesel catalyzed by functionalized dication ionic liquid. *Acta. Agric. Univ. Jiangxiensis.* **38** (2016) 386–390.
 11. Xiong, W. M.; Chen, J.; Peng, D. Y.; Nie, X. L.; Huang, C. G.: Crystal structure of 1,1'-butanebis(3-methyl-1*H*-imidazol-3-ium), bis(hexafluorophosphate), $C_{12}H_{20}F_{12}N_4P_2$. *Kristallogr. NCS.* **232** (2017) 1007–1008.
 12. Nie, X. L.; Kong, J. H.; Chen, J.; Chen, J. Z.; Xiong, W. M.: Crystal structure of 1,1'-(hexane-1,6-diyl)bis(3-methyl-1*H*-imidazol-3-ium), bis(hexafluorophosphate), $C_9H_{14}F_{12}N_4P_2$. *Kristallogr. NCS.* **232** (2017) 73–74.
 13. Xiong, W. M.; Zhou, L.; Lv, S. M.; Nie, X. L.; Chen, J.; Huang, C. G.: Crystal structure of 1,1'-(pentane-1,5-diyl)bis(3-methyl-1*H*-imidazol-3-ium), bis(hexafluorophosphate), $C_9H_{14}F_{12}N_4P_2$. *Kristallogr. NCS.* **233** (2018) 473–474.
 14. Xiong, W. M.; Di, Y. B.; Lan, Y. D.; Chen, J.; Nie, X. L.; Huang, C. G.: Crystal structure of 1,1'-(ethane-1,2-diyl)bis(3-ethyl-1*H*-imidazol-3-ium), bis(hexafluorophosphate), $C_{12}H_{20}F_{12}N_4P_2$. *Kristallogr. NCS.* **234** (2019) 473–474.