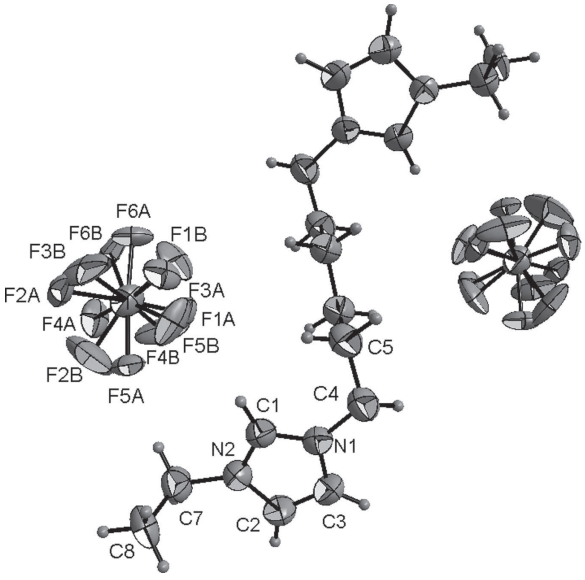
Zhao Wen, Chen Jing, Xiong Wan-Ming*, Lan Ying-Dong and Nie Xu-Liang*

Crystal structure of 1,1′-(hexane-1,6-diyl)bis(3-ethyl-1*H*-imidazol-3-ium) bis(hexafluorido phosphate), $C_{16}H_{28}F_{12}N_4P_2$



https://doi.org/10.1515/ncrs-2018-0527
Received November 23, 2018; accepted January 14, 2019; available online March 26, 2019

Abstract

$C_{16}H_{28}N_4$ 2(F_6P), monoclinic, $P2_1/n$ (no. 14), $a = 8.7921(12)$ Å, $b = 16.173(2)$ Å, $c = 9.1376(12)$ Å, $\beta = 111.13(10)°$, $V = 1211.1(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0475$, $wR_{ref}(F^2) = 0.1262$, $T = 296(2)$ K.

CCDC no.: 1890717

***Corresponding authors: Xiong Wan-Ming,** Collaborative Innovation Center of Jiangxi Typical Trees Cultivation and Utilization/Institute of functional materials and agricultural applied chemistry, Jiangxi Agricultural University, Nanchang 330045, People's Republic of China, e-mail: xiongwm10@163.com; and **Nie Xu-Liang,** Key Laboratory of Natural, Product Research and Development/College of Sciences, Jiangxi Agricultural, University, Nanchang 330045, People's Republic of China, e-mail: niexuliang1981@163.com
Zhao Wen and Chen Jing: College of Sciences, Jiangxi Agricultural University, Nanchang 330045, People's Republic of China
Lan Ying-Dong: Collaborative Innovation Center of Jiangxi Typical Trees Cultivation and Utilization/College of Sciences, Jiangxi Agricultural University, Nanchang 330045, People's Republic of China

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.13 × 0.12 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.28 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8792, 2125, 0.025
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1691
$N(param)_{refined}$:	214
Programs:	Bruker [1], SHELX [2]

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.

Source of material

1-Ethylimidazole (9.61 g, 0.1 mol) was dissolved in methylbenzene (20 mL), 1,6-dibromohexane (12.1 g, 0.05 mol) was quickly added under stirring. The mixture was reacted at 80 °C for 10 min, and then heated to 90 °C for 8 hours. After the reaction completed (monitored by TLC), a white solid was produced after cooling. The resulting suspension was filtered, crushed and washed with ethylacetate and diethyl ether 3 times respectively. The white powder intermediate (C6EM—Br) was dryed *in vacuo* (19.32 g, yield 89%). Then the intermediates (C6EM—Br)(2.17 g, 0.005 mol), potassium hexafluoro phosphate (2.48 g, 0.012 mol) was dissolved in water (36 mL) and methanol (4 mL). The mixture stirred well for 12 h at 95 °C and then cooled slowly. The 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 $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for all other H atoms. The $[PF_6]^-$ anion is disordered over two positions (*cf.* the figure, Table 2), which is typical for many hexafluoridophosphates.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.7923(3)	0.12721(14)	0.7499(3)	0.0575(6)
H1	0.7552	0.1365	0.6422	0.069*
C2	0.7987(3)	0.11004(16)	0.9873(3)	0.0672(7)
H2	0.7661	0.1054	1.0730	0.081*
C3	0.9506(3)	0.10413(17)	0.9903(3)	0.0677(7)
H3	1.0435	0.0943	1.0785	0.081*
C4	1.0899(3)	0.11948(17)	0.7957(3)	0.0705(7)
H4A	1.1727	0.0822	0.8619	0.085*
H4B	1.1340	0.1751	0.8149	0.085*
C5	1.0557(3)	0.09795(17)	0.6285(3)	0.0692(7)
H5A	1.1514	0.1112	0.6041	0.083*
H5B	0.9672	0.1327	0.5632	0.083*
C6	1.0109(3)	0.00919(17)	0.5847(3)	0.0653(7)
H6A	0.9103	−0.0035	0.6008	0.078*
H6B	1.0958	−0.0263	0.6533	0.078*
C7	0.5235(3)	0.13844(18)	0.7799(3)	0.0698(7)
H7A	0.4757	0.1041	0.8391	0.084*
H7B	0.4751	0.1227	0.6703	0.084*
C8	0.4863(4)	0.2258(2)	0.7974(5)	0.1031(12)
H8A	0.5316	0.2411	0.9062	0.155*
H8B	0.3701	0.2335	0.7589	0.155*
H8C	0.5328	0.2599	0.7383	0.155*
N1	0.9453(2)	0.11507(11)	0.8413(2)	0.0543(5)
N2	0.6998(2)	0.12405(11)	0.8359(2)	0.0530(5)
P1	0.47114(8)	0.12475(4)	0.26721(7)	0.0611(3)
F1A[a]	0.5814(5)	0.0605(3)	0.3840(5)	0.117(2)
F2A[b]	0.3524(7)	0.1910(4)	0.1550(8)	0.111(2)
F3A[c]	0.6207(8)	0.1665(3)	0.2408(10)	0.120(3)
F4A[d]	0.3188(4)	0.0808(3)	0.2762(8)	0.137(2)
F5A[d]	0.4945(8)	0.1866(2)	0.4046(3)	0.1095(17)
F6A[e]	0.4712(16)	0.0674(5)	0.1278(9)	0.128(3)
F1B[f]	0.609(2)	0.100(3)	0.235(3)	0.236(15)
F2B[g]	0.366(4)	0.1624(16)	0.344(3)	0.299(17)
F3B[h]	0.428(4)	0.1858(10)	0.1385(16)	0.193(13)
F4B[i]	0.502(4)	0.0617(12)	0.397(2)	0.195(17)
F5B[i]	0.631(2)	0.1746(11)	0.358(3)	0.165(12)
F6B[j]	0.389(4)	0.0635(7)	0.140(2)	0.179(10)

[a]Occupancy: 0.779(10), [b]Occupancy: 0.694(14), [c]Occupancy: 0.666(16), [d]Occupancy: 0.770(9), [e]Occupancy: 0.62(2), [f]Occupancy: 0.221(10), [g]Occupancy: 0.306(14), [h]Occupancy: 0.334(16), [i]Occupancy: 0.230(9), [j]Occupancy: 0.38(2).

Comment

Room temperature ionic liquid (RTIL) offer many advantages from an environmental perspective such as being nonflammable and thermally stable, having a negligible vapor pressure, and having the potential for recyclability. Dicationic ionic liquid, with a large variety of tunable interactions, has been explored in the past decade [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 and separation effect of the catalyst was ideal [8].

Recently, our group focused on the preparation of biodiesel catalyzed by ionic liquid [9, 10] and reported three crystal structures of 1,1′-(butane-1,4-diyl)bis(3-methyl-1*H*-imidazol-3-ium), bis(hexafluorophosphate), 1,1′-(hexane-1,6-diyl)bis(3-methyl-1*H*-imidazol-3-ium), bis(hexafluorophosphate) and 1,1′-(ethane-1,2-diyl)bis(3-ethyl-1*H*-imidazol-3-ium), bis(hexafluorophosphate) [11–13]. In order to find the ionic liquid catalyst with better catalytic efficiency, we were engaged in synthesising novel ionic liquid catalysts with imidazole.

Herein, we report the synthesis and structure of the bisimidazoles ionic liquid. Bond lengths and angles within the imidazloe ring are very similar to those given in the literature for diimidazole ionic liquid [14]. The title structure consists of one half of $C2M^{2+}$ cation (1,1′-(ethane-1,2-diyl)bis(3-ethyl-1*H*-imidazol-3-ium)) and one $[PF_6]^-$ anion (*cf.* the figure). Two cationic 1-ethylimidazolium rings were bound to the both sides of ethyl group. The two imidazole rings are crystallographically dependant planar and parallel to each other. The torsion angle of C4—N1—C3—C2, C3—N1—C4—C5 and N1—C4—C5—C6 is 175.1(2)°, 156.7(2)° and 67.5(3)°, respectively.

Acknowledgements: X-ray data were collected at Instrumental Analysis Center Nanchang Hangkong University, Nanchang, 330063, People's Republic of China. This work was supported by the National Natural Science Foundation of China (No. 31760193) and the Research Foundation of Educational Department of Jiangxi Province [GJJ160382, 160379].

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. **A64** (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. J. Energy Chem. **23** (2014) 97–104.
4. Rafiee, E.; Eavani, S.: A new organic – inorganic hybrid ionic liquid polyoxometalate for biodiesel production. J. Mol. Liq. **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. J. Wood Chem. Techn. **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 Fuels **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), $C_{12}H_{20}F_{12}N_4P_2$. Z. 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), $C_9H_{14}F_{12}N_4P_2$. Z. Kristallogr. NCS **232** (2017) 73–74.
13. 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), $C_9H_{14}F_{12}N_4P_2$. Z. Kristallogr. NCS. **234** (2019) 73–74.
14. Li, M.; Niu, Z. B.; Schoonover, D. V.; Slebodnick, C.; Gibson, H. W.: 1,2-Bis(*N*-(*N*′-alkylimidazolium))ethane salts as new guests for crown ethers and cryptands. Tetrahedron **66** (2010) 7077–7082.