Zhao Bo, Zhong Yue and Luo Jiewei*

The crystal structure of 1-(2-(2-(imidazo[1,5-a]pyridine-4-ium)ethoxy)ethyl)-imidazo[1,5-a]pyridine-4-ium bis(hexafluorophosphate) – acetonitrile (1/1), $C_{18}H_{20}ON_4F_{12}P_2$

<https://doi.org/10.1515/ncrs-2019-0572>

Received August 7, 2019; accepted October 2, 2019; available online October 18, 2019

Abstract

$C_{18}H_{20}ON_4F_{12}P_2$, triclinic, $P\bar{1}$ (no. 2), $a = 9.393(8)$ Å, $b = 10.894(10)$ Å, $c = 13.716(12)$ Å, $\alpha = 107.741(14)^\circ$, $\beta = 100.379(15)^\circ$, $\gamma = 92.869(14)^\circ$, $V = 1306.7(19)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0916$, $wR_{ref}(F^2) = 0.1970$, $T = 296(2)$ K.

CCDC no.: 1957190

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.

*Corresponding author: Luo Jiewei, North Sichuan Medical College, School of Basic Medical Sciences, Nanchong 637000, P.R. China, e-mail: luojiewei198021@163.com

Zhao Bo and Zhong Yue: North Sichuan Medical College, School of Basic Medical Sciences, Nanchong 637000, P.R. China. <https://orcid.org/0000-0003-0987-7602> (Z. Bo)

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	$0.28 \times 0.24 \times 0.21$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.28 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	26.0° , 98%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7070, 5041, 0.021
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3424
$N(\text{param})_{\text{refined}}$:	362
Programs:	Bruker [1], SHELX [2, 3]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
P1	0.98375(16)	0.63041(14)	0.23466(11)	0.0584(4)
P2	0.46505(16)	0.28564(16)	0.25893(12)	0.0612(4)
C1	0.2475(6)	0.8786(6)	0.5351(4)	0.0629(14)
H1A	0.2429	0.8153	0.5674	0.075*
C2	0.1795(6)	0.9846(6)	0.5638(4)	0.0638(15)
H2A	0.1285	0.9953	0.6174	0.077*
C3	0.1836(6)	1.0806(6)	0.5146(4)	0.0628(14)
H3A	0.1349	1.1533	0.5359	0.075*
C4	0.2572(6)	1.0680(5)	0.4372(4)	0.0577(13)
H4A	0.2587	1.1312	0.4045	0.069*
C5	0.3317(5)	0.9586(5)	0.4061(3)	0.0445(10)
C6	0.4161(5)	0.9168(5)	0.3336(4)	0.0532(12)
H6A	0.4401	0.9596	0.2886	0.064*
C7	0.4038(6)	0.7708(5)	0.4126(4)	0.0570(13)
H7A	0.4177	0.6962	0.4310	0.068*
C8	0.5481(6)	0.7222(6)	0.2722(4)	0.0698(16)
H8A	0.5966	0.6664	0.3075	0.084*
H8B	0.6223	0.7782	0.2606	0.084*
C9	0.4575(7)	0.6411(6)	0.1694(4)	0.0687(16)
H9A	0.5157	0.5806	0.1308	0.082*
H9B	0.3766	0.5917	0.1805	0.082*
C10	0.3182(7)	0.6503(5)	0.0138(4)	0.0669(15)
H10A	0.2409	0.5956	0.0235	0.080*
H10B	0.3775	0.5949	−0.0281	0.080*
C11	0.2538(6)	0.7404(6)	−0.0418(4)	0.0656(15)
H11A	0.3299	0.8050	−0.0401	0.079*
H11B	0.2131	0.6916	−0.1144	0.079*
C12	−0.0005(6)	0.7586(5)	−0.0179(4)	0.0599(13)
H12A	−0.0412	0.6805	−0.0686	0.072*
C13	0.1587(6)	0.9222(5)	0.0839(4)	0.0540(12)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H13A	0.2465	0.9747	0.1143	0.065*
C14	0.0270(5)	0.9480(5)	0.1081(3)	0.0492(11)
C15	−0.0254(7)	1.0511(6)	0.1782(4)	0.0637(15)
H15A	0.0385	1.1219	0.2231	0.076*
C16	−0.1679(7)	1.0460(7)	0.1797(5)	0.0745(18)
H16A	−0.2027	1.1145	0.2251	0.089*
C17	−0.2655(7)	0.9389(8)	0.1136(5)	0.081(2)
H17A	−0.3636	0.9372	0.1168	0.098*
C18	−0.2206(7)	0.8397(7)	0.0466(5)	0.0750(17)
H18A	−0.2862	0.7692	0.0033	0.090*
C20	0.9042(8)	0.6280(7)	0.5665(5)	0.0747(17)
F1	1.0479(9)	0.6627(6)	0.3484(4)	0.204(4)
F2	0.8493(7)	0.5653(9)	0.2505(7)	0.226(4)
F3	0.9191(9)	0.7599(6)	0.2546(6)	0.205(3)
F4	0.9248(10)	0.5974(6)	0.1186(4)	0.224(4)
F5	1.1098(7)	0.7115(7)	0.2189(5)	0.181(3)
F6	1.0356(11)	0.5017(6)	0.2133(6)	0.244(5)
F7	0.4714(7)	0.2580(6)	0.3636(4)	0.155(2)
F8	0.2977(5)	0.2583(6)	0.2331(5)	0.153(2)
F9	0.4601(6)	0.4319(4)	0.3194(4)	0.1268(17)
F10	0.6357(4)	0.3052(5)	0.2833(4)	0.1277(17)
F11	0.4714(6)	0.1394(4)	0.1975(5)	0.144(2)
F12	0.4669(6)	0.3174(6)	0.1571(4)	0.1410(19)
N1	0.3256(4)	0.8648(4)	0.4554(3)	0.0521(10)
N2	0.4579(4)	0.8025(4)	0.3393(3)	0.0511(10)
N3	−0.0719(5)	0.8437(4)	0.0428(3)	0.0568(11)
N4	0.1389(5)	0.8058(4)	0.0075(3)	0.0526(10)
O1	0.4045(4)	0.7233(3)	0.1117(3)	0.0572(9)
C19	0.7867(9)	0.5302(8)	0.5119(7)	0.118(3)
H19A	0.6968	0.5685	0.5101	0.177*
H19B	0.7846	0.4663	0.5468	0.177*
H19C	0.7991	0.4898	0.4417	0.177*
N5	0.9969(8)	0.7058(7)	0.6081(5)	0.105(2)

Source of material

The title compound was synthesized by the reaction of 2-(2-amino-ethoxy)-ethanamine (0.29 mL, 2 mmol), formalin (0.58 mL, 6 mmol) and picolinaldehyde (0.38 mL, 4 mmol) in ethanol [4]. Hydrogen bromide (2 equiv) was added to the reaction mixture, which was stirred at room temperature for 12 h. Following salt metathesis with NH₄PF₆ in acetonitrile, a yellow solid was obtained, 0.98 g. Yield: 82%. ¹H NMR (400 MHz, DMSO) δ [ppm] 9.62 (s, 2H), 8.54–8.45 (m, 2H), 8.13 (s, 2H), 7.75 (d, *J* = 9.3 Hz, 2H), 7.28–7.11 (m, 4H), 4.67 (t, *J* = 4.8 Hz, 4H), 3.90 (t, *J* = 4.8 Hz, 4H). ¹³C NMR (100 MHz, DMSO) δ [ppm] 129.40, 127.09, 125.04, 124.47, 118.49, 117.92, 114.05, 68.55, 50.36.

Experimental details

The structure was solved by Direct Methods. The largest residual density peaks are near the PF₆ anions indicating a small additional disorder of these ions.

Comment

Despite a massive number of NHCs were reported using a variety of synthetic methods [5, 6], it remains a challenge to get NHCs with tunable electronic and steric properties. Many NHCs containing the imidazo[1,5-*a*]pyridine have been synthesized [7–11].

Geometric parameters in the title molecule are in the expected ranges. In detail the bond lengths of O1-C9 and O1-C10 are 1.419(6) and 1.409(6) Å, respectively, and the angle of C9-O1-C10 is 110.8(4)°. The supramolecular assembly in title compound depends on the combination of C-H...F hydrogen-bonding and π-π stacking. The imidazolium cation and hexafluoro phosphate anions are connected by C-H...F hydrogen-bond (d(H acceptor) and d(donor... acceptor), donor-H... acceptor): C12-H12A... F6ⁱ (2.35, 3.207(8) Å), 153.0°; C13-H13A... F11ⁱⁱ (2.55, 3.473(8) Å), 173.8°; C18-H18A... F12ⁱⁱⁱ (2.42, 3.232(9) Å), 146.4°. Symmetry codes: *i* = −*x* + 1, −*y* + 1, −*z*; *ii* = *x*, 1 + *y*, *z*; *iii* = −*x*, 1 − *y*, −*z*. In the π-π stacking, the aromatic rings of the molecules, which are strictly parallel, have an inter-planar spacing of 3.603(2) and 3.599(2) Å, respectively.

Acknowledgements: We gratefully acknowledge support by Project of Nanchong Science and Technology Bureau (18SXHZ0133); University Innovation and Entrepreneurship Training Program of Sichuan (106342018146).

References

1. Bruker. SAINT-Plus, SHELXTL and SADABS. Bruker AXS Inc., Madison, WI, USA (2013).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **71** (2015) 3–122.
4. Hutt, J. T.; Aron, Z. D.: Efficient, single-step access to imidazo[1,5-*a*]pyridine *n*-heterocyclic carbene precursors. *Org. Lett.* **13** (2011) 5256–5259.
5. Huynh, H. V.: Electronic properties of *N*-heterocyclic carbenes and their experimental determination. *Chem. Rev.* **118** (2018) 9457–9492.
6. Vivancos, A.; Segarra, C.; Albrecht, M.: Mesoionic and related less heteroatom-stabilized *N*-heterocyclic carbene complexes: synthesis, catalysis, and other applications. *Chem. Rev.* **118** (2018) 9493–9586.
7. Azouzi, K.; Duhayon, C.; Benaissa, I.; Lugan, N.; Canac, Y.; Bastin, S.; Cesar, V.: Bidentate iminophosphorane-NHC ligand and derived from the imidazo[1,5-*a*]pyridin-3-ylidene scaffold. *Organometallics* **37** (2018) 4726–4735.
8. Zhao, B.; Zhang, S.: The crystal structure of 9-butoxy-2-(hydroxymethyl)-2*H*-imidazo[1,5-*a*]quinolin-10-ium bromide. *Z. Kristallogr. NCS* **233** (2018) 1069–1070.
9. Alcarazo, M.; Rosenblade, S. J.; Cowley, A. R.; Fernandez, R.; Brown, J. M.; Lassaletta, J. M.: Imidazo[1,5-*a*]pyridine: a versatile architecture for stable *N*-heterocyclic carbenes. *J. Am. Chem. Soc.* **127** (2005) 3290–3293.

10. Teresa, K. M.; Jens, W. K.; Korbinian, R.; Alexander, P.; Wolfgang, A. H.; Fritz, E. K.: Decoding catalytic activity of platinum carbene hydrosilylation catalysts. *J. Catal.* **337** (2016) 157–166.
11. Zhao, B.; Zhang, H. L.; Tang, W.; Yuan, W. G.; Xiong, F.; Jing, L. H.; Qin, D. B.: Structure of co-crystals formation from imidazolium and aromatic ligands. *Chin. J. Struct. Chem.* **33** (2014) 415–421.