

Mouslim Messali, Mohamed Reda Aouad*, Nadjat Rezki, M. Saud Almutairi and Ismail Warad*

Crystal structure of 4-(dimethylamino)-1-(prop-2-yn-1-yl)pyridin-1-ium perchlorate, $C_{10}H_{13}ClN_2O_4$

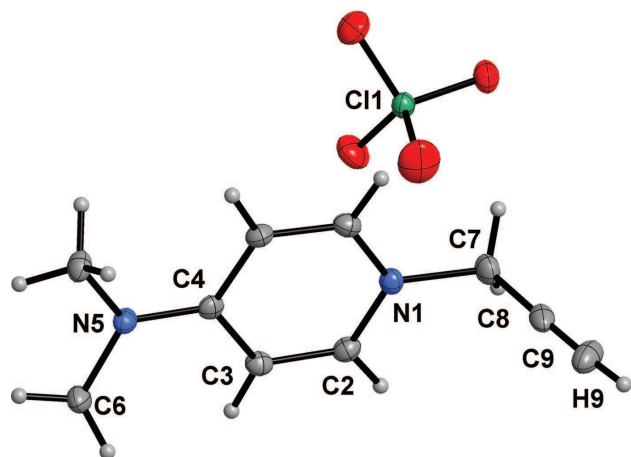


Table 1: Data collection and handling.

Crystal:	White rectangle
Size:	$0.29 \times 0.28 \times 0.25$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ :	2.93 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
θ_{max} , completeness:	66.6° , 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13090, 1111, 0.036
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1100
$N(\text{param})_{\text{refined}}$:	118
Programs:	Bruker [1], SHELX [2]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.49400(11)	0.75000	0.82061(17)	0.0157(5)
N5	0.24578(10)	0.75000	1.03169(18)	0.0162(4)
C2	0.45244(9)	0.62124(15)	0.85399(16)	0.0168(4)
C3	0.37034(8)	0.61741(14)	0.92154(15)	0.0161(4)
C4	0.32557(12)	0.75000	0.9613(2)	0.0145(5)
C6	0.20502(9)	0.61205(16)	1.08245(17)	0.0206(4)
C7	0.58436(13)	0.75000	0.7511(2)	0.0206(6)
C8	0.65587(13)	0.75000	0.8658(3)	0.0202(6)
C9	0.71497(15)	0.75000	0.9564(3)	0.0278(7)
Cl1	0.44177(3)	0.75000	0.32656(5)	0.0172(2)
O1	0.51313(9)	0.75000	0.21559(17)	0.0237(4)
O2A ^a	0.38674(8)	0.62130(12)	0.30292(13)	0.0284(3)
O2B ^b	0.4642(16)	0.875(3)	0.439(3)	0.0284(3)
O3A ^a	0.47763(12)	0.75000	0.47677(19)	0.0408(6)
O3B ^b	0.355(3)	0.75000	0.303(4)	0.0408(6)
H2	0.4840(11)	0.535(2)	0.8268(17)	0.0200*
H3	0.3446(10)	0.527(2)	0.9418(18)	0.0190*
H6A	0.1955(12)	0.548(2)	0.996(2)	0.0310*
H6B	0.1482(13)	0.634(2)	1.125(2)	0.0310*
H6C	0.2438(13)	0.566(2)	1.155(2)	0.0310*
H7	0.5872(12)	0.6688(19)	0.6883(18)	0.0250*
H9	0.761(2)	0.75000	1.019(4)	0.051(9)*

^aOccupancy: 0.954(2), ^bOccupancy: 0.046(2).

<https://doi.org/10.1515/ncrs-2018-0084>

Received April 10, 2018; accepted June 18, 2018; available online July 7, 2018

Abstract

$C_{10}H_{13}ClN_2O_4$, orthorhombic, $Pnma$, $a = 14.903(2)$ Å, $b = 9.1004(15)$ Å, $c = 8.7560(14)$ Å, $V = 1187.5(3)$ Å³, $Z = 4$, $R_{\text{int}} = 0.036$, $R_{\text{gt}}(F) = 0.0284$, $wR_{\text{ref}}(F^2) = 0.0795$, $T = 296$ K.

CCDC no.: 1824879

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

The 4-(dimethylamino)-1-(prop-2-yn-1-yl)pyridin-1-ium iodide (1 eq) was dissolved in dichloromethane to obtain a clear solution. To this solution was added a solution of potassium perchlorate (1.2 eq), followed by stirring under reflux for 3 h. The cooled reaction mixture was filtered through

Celite to remove solid metal halide. The evaporation of dichloromethane led quantitatively to the desired 4-(dimethylamino)-1-(prop-2-yn-1-yl)pyridin-1-ium perchlorate ($C_{10}H_{13}N_2$)[ClO₄]. Single crystals were obtained from a mixture of dichloromethane and n-hexane (1:2).

*Corresponding authors: **Mohamed Reda Aouad**, Department of Chemistry, Taibah University, 30002 Al-Madina Al-Mounawara, Saudi Arabia, e-mail: aouadmohamedreda@yahoo.fr; and **Ismail Warad** Department of Chemistry, AN-Najah National University, P.O. Box 7, Nablus, Palestine, e-mail: warad@najah.edu (I. Warad) **Mouslim Messali and Nadjat Rezki**: Department of Chemistry, Taibah University, 30002 Al-Madina Al-Mounawara, Saudi Arabia **M. Saud Almutairi**: King Abdulaziz City for Science and Technology, P.O.Box 6086, Riyadh 11442, Saudi Arabia

Experimental details

Hydrogen atoms were placed at the calculated positions and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ or $1.5 U_{\text{eq}}$ of the adjacent non-hydrogen atom. The H9 atom (propynyl group) position was localized from the difference map and refined with $\text{DFIX } 0.87$ and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O}3)$ [1, 2]. The perchlorate anion shows a disorder (not shown in the figure).

Comment

Pyrimidine salt and its derivatives are pharmaceutically essential since they occur in nucleic acid system, therefore many pyrimidine-derivatives salts can served as drugs [3]. Given the importance of pyrimidine derivatives in some bio-systems, a lot of interest has been concentrated on such stable salt recently [4]. Because of the basic nitrogen-atoms in the backbone of pyrimidine derivatives it was used as proton-receptor or ligand [5]. Perchlorate anions are used as ligands for the elaboration of metal complexes having interesting applications in various fields [5–9]. Several organic cations can be used for the stabilization of these anions especially benzylammonium and pyrimidinium derivatives [9–11].

In the cation of the title salt the pyridinium ring and dimethyl amine group is approximately co planar, which may be supported by lone pair of N (NMe₂). The propyne group is in semi-perpendicular plane to the pyridinium rings with 112° angle value. Moreover the propynyl is in the opposite direction of the perchlorate anion in order to minimize the repulsion.

References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA (2012).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Hitching, G. H.; Kuyper, L. F.; Baccanari, D. P.: Design of enzyme inhibitors as drugs, ed., Sandler, M., Smith, H. J.: Oxford University Press, New York (1988) 343.
4. Mitra, A.; Banerjee, T.; Roychowdhury, P.; Saha, N.; Das, S.: X-ray crystal structure of bis-(p-nitroacetophenone-4,6-dimethyl-2-pyrimidyl-hydrazone) copper(I) perchlorate. *Polyhedron* **15** (1996) 3371–3375.
5. Hu, Y.-M.; Qu, J.; Yi, Y.-L.; Gao, H.-L.; Cui, J.-Z.: Syntheses, crystal structures, and properties of four transition metal complexes based on 5-nitro-8-hydroxyquinoline. *J. Coord. Chem.* **66** (2013) 18–27.
6. Gao, H.-L.; Jiang, S.-X.; Hu, Y.-M.; Li, F.-F.; Zhang, Q.-Q.; Shi, X.-Y.; Cui, J.-Z.: Syntheses, structures and luminescent properties of the metal complexes based on Zn(II) or Cd(II) with 5-nitro-8-hydroxyquinoline. *Inorg. Chem. Commun.* **44** (2014) 58–62.
7. Zhang, H.-R.; Huang, K.-B.; Chen, Z.-F.; Liu, Y.-C.; Liu, Y.-N.; Meng, T.; Qin, Q.-P.; Zou, B.-Q.; Liang, H.: Cobalt(II) 8-hydroxyquinoline complexes: structure, cytotoxicity and action mechanism. *Med. Chem. Commun.* **7** (2016) 806–812.
8. Zhao, G.: Crystal structure of (8-hydroxy-5-nitroquinolinium) perchlorate-8-hydroxy-5-nitroquinoline (1/1), C₁₈H₁₃ClN₄O₁₀. *Z. Kristallogr. NCS* **232** (2017) 689–691.
9. Czupinski, O.; Bator, G.; Ciunik, Z.; Jakubas, R.; Medycki, W.; Swiergiel, J.: Structure, phase transitions and molecular motions in 4-aminopyridinium perchlorate. *J. Phys.: Condens. Matter* **14** (2002) 8497–8512.
10. Czupinski, O.; Wojtas, M.; Zaleski, J.; Jakubas, R.; Medycki, W.: Structure and properties of 2-cyanopyridinium perchlorate [2-CNPyH][ClO₄]. *J. Phys.: Condens. Matter* **18** (2006) 3307–3324.
11. Vollano, J. F.; Day, R. O.; Rau, D. N.; Chadrasekhar, V.; Holmes, R. R.: Pentacoordinated molecules, intramolecularly formed pentacoordinated structures of triphenyltin esters of salicylic acid, o-anisic acid, and p-methylthiobenzoic acid. *Inorg. Chem.* **23** (1984) 3153–3160.