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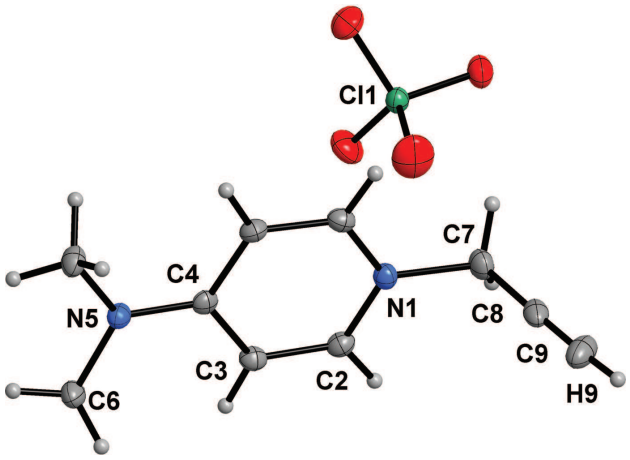
Crystal structure of 4-(dimethylamino)-1-(prop-2-yn-1-yl)pyridin-1-ium perchlorate, $C_{10}H_{13}ClN_2O_4$



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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, $V = 1187.5(3)$ Å^3, $Z = 4$, $R_{int} = 0.036$, $R_{gt}(F) = 0.0284$, $wR_{ref}(F^2) = 0.0795$, $T = 296$ 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.

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 ($C_{10}H_{13}N_2$)[ClO_4]. Single crystals were obtained from a mixture of dichloromethane and n-hexane (1:2).

Table 1: Data collection and handling.

Crystal:	White rectangle
Size:	0.29 × 0.28 × 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%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13090, 1111, 0.036
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1100
$N(param)_{refined}$:	118
Programs:	Bruker [1], SHELX [2]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{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)*

[a]Occupancy: 0.954(2), [b]Occupancy: 0.046(2).

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Experimental details

Hydrogen atoms were placed at the calculated positions and refined using a riding model with $U_{iso}(H) = 1.2\ U_{eq}$ or $1.5\ U_{eq}$ of the adjacent non-hydrogen atom. The H9 atom (propynyl group) position was localized from the difference map and refined with DFIX 0.87 and $U_{iso}(H) = 1.5\ U_{eq}(O3)$ [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 biosystems, 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 (NMe_2). 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.

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