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3-Cyano-*N*-methylpyridinium perchlorate

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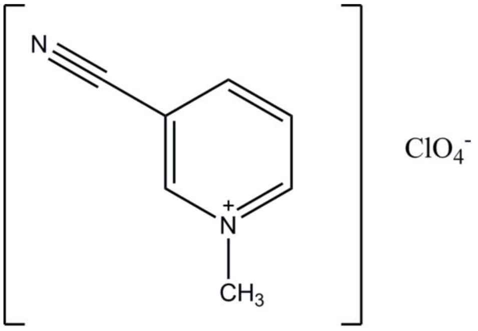
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.002 Å; R factor = 0.032; wR factor = 0.089; data-to-parameter ratio = 18.5.

In the crystal of the title molecular salt, $C_7H_7N_2^+\cdot ClO_4^-$, the components are linked by C—H⋯O and C—H⋯N interactions, generating zigzag chains running parallel to [100].

Related literature

For structures of other 3-cyano-1-methylpyridinium salts, see: Koplitz *et al.* (2003); Mague *et al.* (2005); Zhu *et al.* (1999). For the structure of 4-cyano-1-methylpyridinium perchlorate, see: Nguyen *et al.* (2014). For a discussion of anion–π interactions, see: Frontera *et al.* (2011). In contrast to the structure found for the title compound, the structures of the isomeric salts 2-cyano-1-methylpyridinium nitrate (Koplitz *et al.*, 2003) and 2-cyanoanilinium nitrate (Cui & Wen, 2008) crystallize in flat layers of two-dimensional networks with only a few atoms protruding from the mirror plane while 3-cyanoanilinium nitrate (Wang, 2009) forms a more open structure.



Experimental

Crystal data

$C_7H_7N_2^+\cdot ClO_4^-$
M_r = 218.60
Monoclinic, $P2_1/c$
a = 8.1490 (7) Å
b = 7.7338 (7) Å
c = 14.5297 (13) Å
β = 97.522 (1)°
V = 907.82 (14) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.41 mm^{-1}
T = 120 K
0.26 × 0.24 × 0.05 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2010)
T_{min} = 0.89, T_{max} = 0.98
15448 measured reflections
2364 independent reflections
2187 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.089
S = 1.10
2364 reflections
128 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C1—H1A⋯O2^{i}	0.98	2.56	3.5377 (19)	173
C1—H1A⋯O3^{i}	0.98	2.59	3.1868 (17)	119
C1—H1B⋯N2^{ii}	0.98	2.56	3.3136 (19)	134
C1—H1B⋯O2	0.98	2.62	3.3759 (17)	134
C2—H2⋯O1^{iii}	0.95	2.22	3.1577 (16)	168

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $x-1, y, z$; (iii) $x+1, y, z$.

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2012); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7237).

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supporting information

Acta Cryst. (2014). E**70**, o811 [https://doi.org/10.1107/S1600536814014421]

3-Cyano-*N*-methylpyridinium perchlorate

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S1. Comment

A perspective view of the title compound appears in Fig. 1 while Fig. 2 illustrates the zigzag rows of anions with cations bound on either side *via* C—H···O hydrogen bonds (Table 1). Additionally, there are C—H···N interactions between methyl H atoms of one cation and the cyano group of the next cation in the chain. An end view of these motifs is shown in Fig. 3. A notable feature is the close cation-anion contact (H1A···O2^{i} = 2.56 Å (symmetry code: (i) 1 - *x*, -*y*, 1 - *z*) which is strikingly similar to the motif that dominates the structure of 2-cyano-1-methylpyridinium nitrate (Koplitz *et al.*, 2003). These close contacts are likely the result of electrostatic cation-anion attraction with the orientation possibly reinforced by an anion-π interaction (Frontera *et al.*, 2011). In contrast to the structure found for the title compound, the structures of the isomeric salts 2-cyano-1-methylpyridinium nitrate (Koplitz *et al.*, 2003) and 2-cyanoanilinium nitrate (Cui & Wen, 2008) crystallize in flat layers of two-dimensional networks with only a few atoms protruding from the mirror plane while 3-cyanoanilinium nitrate (Wang, 2009) forms a more open structure.

S2. Experimental

3-Cyanopyridine (10.55 g) was dissolved in benzene (40 ml). Iodomethane (9.5 ml) was added to this solution slowly with stirring and the solution was refluxed for 75 minutes. Yellow solid 3-cyano-1-methylpyridinium iodide (m.p. 196° C, blood-red melt) was collected by vacuum filtration. This solid (0.98 g) was then dissolved in a solution of silver perchlorate previously prepared by reacting Ag_2O (0.47 g) with 0.5 *M* aqueous $HClO_4$(8.0 ml). After stirring, precipitated AgI was removed by vacuum filtration and the filtrate containing 3-cyano-1-methylpyridinium perchlorate was slowly evaporated to dryness to form colorless plates of the title compound.

S3. Refinement

H-atoms were placed in calculated positions (C—H = 0.95 - 0.98 Å) and included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached carbon atoms.

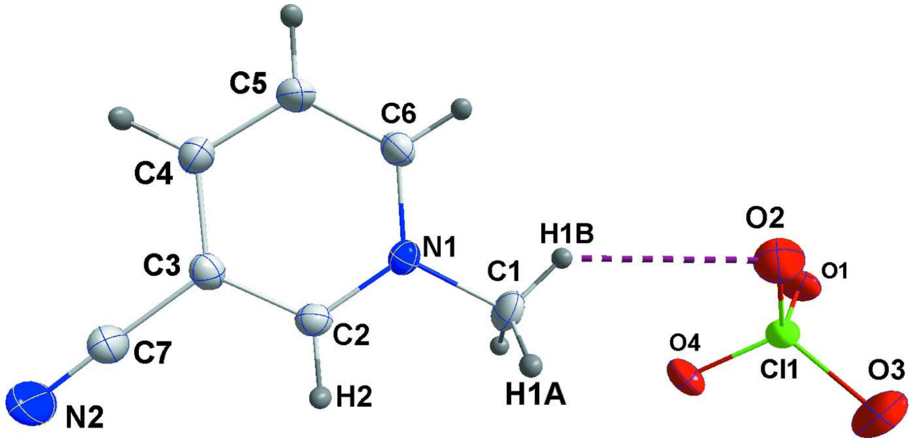

Figure 1

Perspective view of I with displacement ellipsoids drawn at the 50% probability level and H-atoms as spheres of arbitrary radius.

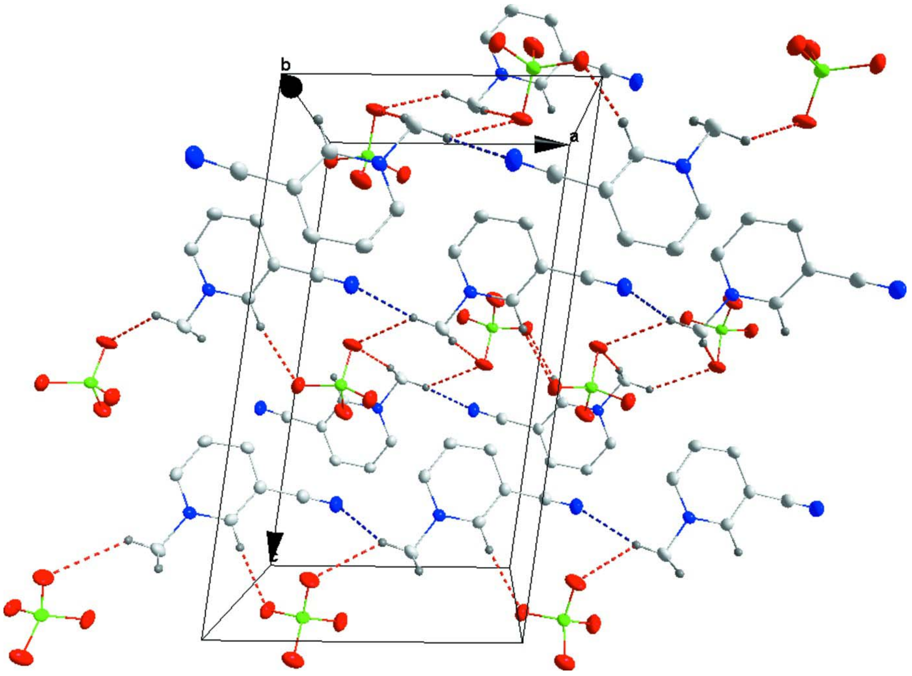

Figure 2

Packing projected down the *b* axis with C—H···O interactions shown as red dotted lines and C—H···N interactions as blue dotted lines.

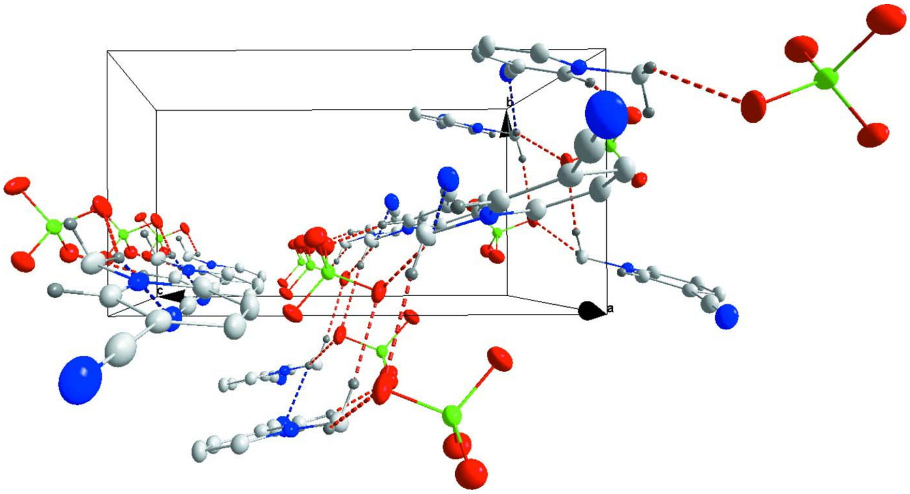

Figure 3

Packing projected onto (100) with C—H···O interactions shown as red dotted lines and C—H···N interactions as blue dotted lines.

3-Cyano-*N*-methylpyridinium perchlorate

Crystal data

$C_7H_7N_2^+\cdot ClO_4^-$	$F(000) = 448$
$M_r = 218.60$	$D_x = 1.599$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.1490$ (7) Å	Cell parameters from 9885 reflections
$b = 7.7338$ (7) Å	$\theta = 2.5$–$29.1°$
$c = 14.5297$ (13) Å	$\mu = 0.41$ mm^{-1}
$\beta = 97.522$ (1)°	$T = 120$ K
$V = 907.82$ (14) Å^3	Plate, colourless
$Z = 4$	0.26 × 0.24 × 0.05 mm

Data collection

Bruker SMART APEX CCD diffractometer	15448 measured reflections
Radiation source: fine-focus sealed tube	2364 independent reflections
Graphite monochromator	2187 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.031$
Absorption correction: multi-scan (*SADABS*; Bruker, 2010)	$\theta_{\text{max}} = 29.1°$, $\theta_{\text{min}} = 2.5°$
$T_{\text{min}} = 0.89$, $T_{\text{max}} = 0.98$	$h = -11\rightarrow11$
	$k = -10\rightarrow10$
	$l = -19\rightarrow19$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.032$	H-atom parameters constrained
$wR(F^2) = 0.089$	$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.4231P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{\text{max}} = 0.001$
2364 reflections	$\Delta\rho_{\text{max}} = 0.33$ e Å^{-3}
128 parameters	$\Delta\rho_{\text{min}} = -0.42$ e Å^{-3}
0 restraints	
Primary atom site location: structure-invariant direct methods	

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5 °. in omega, colllected at phi = 0.00, 90.00 and 180.00 °. and 2 sets of 800 frames, each of width 0.45 ° in phi, collected at omega = -30.00 and 210.00 °. The scan time was 15 sec/frame.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger. H-atoms were placed in calculated positions (C—H = 0.95 - 0.98 Å) and included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached carbon atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
N1	0.67687 (13)	0.33669 (13)	0.36093 (7)	0.0178 (2)
N2	1.23923 (15)	0.4848 (2)	0.35273 (9)	0.0343 (3)
C1	0.58669 (16)	0.28809 (18)	0.43927 (9)	0.0243 (3)
H1A	0.6309	0.1789	0.4663	0.036*
H1B	0.4687	0.2743	0.4167	0.036*
H1C	0.6008	0.3790	0.4867	0.036*
C2	0.84053 (15)	0.36279 (16)	0.37864 (9)	0.0197 (2)
H2	0.8961	0.3454	0.4396	0.024*
C3	0.92864 (15)	0.41495 (16)	0.30835 (9)	0.0193 (2)
C4	0.84807 (16)	0.43730 (17)	0.21847 (9)	0.0215 (3)
H4	0.9072	0.4724	0.1695	0.026*
C5	0.67914 (16)	0.40673 (19)	0.20269 (9)	0.0240 (3)
H5	0.6210	0.4197	0.1420	0.029*
C6	0.59519 (15)	0.35749 (17)	0.27498 (9)	0.0212 (2)
H6	0.4791	0.3382	0.2640	0.025*
C7	1.10263 (16)	0.45190 (19)	0.33204 (9)	0.0246 (3)
Cl1	0.21118 (3)	0.17038 (4)	0.56832 (2)	0.01789 (10)
O1	0.05612 (12)	0.26105 (14)	0.56747 (7)	0.0284 (2)
O2	0.22598 (14)	0.10417 (15)	0.47740 (7)	0.0338 (3)
O3	0.21765 (14)	0.02981 (14)	0.63375 (7)	0.0342 (3)
O4	0.34636 (12)	0.28745 (14)	0.59632 (8)	0.0298 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0195 (5)	0.0164 (5)	0.0182 (5)	0.0014 (4)	0.0051 (4)	0.0010 (4)
N2	0.0211 (6)	0.0475 (8)	0.0342 (7)	0.0006 (5)	0.0028 (5)	0.0047 (6)
C1	0.0247 (6)	0.0263 (6)	0.0239 (6)	0.0022 (5)	0.0109 (5)	0.0051 (5)
C2	0.0198 (6)	0.0207 (6)	0.0182 (5)	0.0024 (4)	0.0008 (4)	0.0013 (4)
C3	0.0170 (5)	0.0191 (5)	0.0218 (6)	0.0022 (4)	0.0029 (4)	0.0007 (4)
C4	0.0216 (6)	0.0257 (6)	0.0180 (5)	0.0014 (5)	0.0058 (4)	0.0006 (5)

C5	0.0223 (6)	0.0323 (7)	0.0170 (5)	0.0007 (5)	0.0006 (4)	−0.0006 (5)
C6	0.0174 (5)	0.0243 (6)	0.0215 (6)	−0.0008 (4)	0.0013 (4)	−0.0024 (5)
C7	0.0205 (6)	0.0301 (7)	0.0235 (6)	0.0023 (5)	0.0038 (5)	0.0032 (5)
Cl1	0.01977 (16)	0.01840 (16)	0.01568 (16)	0.00044 (9)	0.00301 (10)	−0.00022 (9)
O1	0.0199 (4)	0.0324 (5)	0.0315 (5)	0.0058 (4)	−0.0013 (4)	0.0000 (4)
O2	0.0450 (6)	0.0383 (6)	0.0199 (5)	−0.0080 (5)	0.0118 (4)	−0.0091 (4)
O3	0.0465 (6)	0.0273 (5)	0.0317 (5)	0.0102 (5)	0.0160 (5)	0.0121 (4)
O4	0.0216 (5)	0.0303 (5)	0.0359 (6)	−0.0040 (4)	−0.0018 (4)	−0.0065 (4)

Geometric parameters (Å, º)

N1—C2	1.3401 (16)	C3—C7	1.4431 (17)
N1—C6	1.3457 (16)	C4—C5	1.3860 (18)
N1—C1	1.4819 (16)	C4—H4	0.9500
N2—C7	1.1430 (18)	C5—C6	1.3799 (18)
C1—H1A	0.9800	C5—H5	0.9500
C1—H1B	0.9800	C6—H6	0.9500
C1—H1C	0.9800	Cl1—O2	1.4365 (10)
C2—C3	1.3832 (17)	Cl1—O3	1.4406 (10)
C2—H2	0.9500	Cl1—O4	1.4427 (10)
C3—C4	1.3935 (17)	Cl1—O1	1.4437 (10)

C2—N1—C6	121.27 (11)	C5—C4—H4	121.0
C2—N1—C1	118.15 (11)	C3—C4—H4	121.0
C6—N1—C1	120.56 (11)	C6—C5—C4	120.12 (12)
N1—C1—H1A	109.5	C6—C5—H5	119.9
N1—C1—H1B	109.5	C4—C5—H5	119.9
H1A—C1—H1B	109.5	N1—C6—C5	120.34 (12)
N1—C1—H1C	109.5	N1—C6—H6	119.8
H1A—C1—H1C	109.5	C5—C6—H6	119.8
H1B—C1—H1C	109.5	N2—C7—C3	177.92 (16)
N1—C2—C3	120.12 (11)	O2—Cl1—O3	109.73 (7)
N1—C2—H2	119.9	O2—Cl1—O4	109.28 (6)
C3—C2—H2	119.9	O3—Cl1—O4	109.08 (7)
C2—C3—C4	120.11 (11)	O2—Cl1—O1	110.12 (7)
C2—C3—C7	118.06 (11)	O3—Cl1—O1	109.18 (6)
C4—C3—C7	121.78 (11)	O4—Cl1—O1	109.44 (6)
C5—C4—C3	118.02 (11)		

C6—N1—C2—C3	1.11 (18)	C7—C3—C4—C5	−176.95 (13)
C1—N1—C2—C3	−177.46 (11)	C3—C4—C5—C6	0.7 (2)
N1—C2—C3—C4	−1.25 (19)	C2—N1—C6—C5	−0.06 (19)
N1—C2—C3—C7	176.16 (12)	C1—N1—C6—C5	178.47 (12)
C2—C3—C4—C5	0.36 (19)	C4—C5—C6—N1	−0.8 (2)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···O2^{i}	0.98	2.56	3.5377 (19)	173
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