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3-Hydroxy-2-(hydroxymethyl)pyridinium chloride

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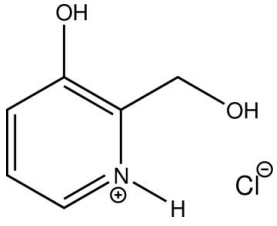
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.002 Å; R factor = 0.025; wR factor = 0.073; data-to-parameter ratio = 16.6.

The cation of the title compound, $C_6H_8NO_2^+\cdot Cl^-$, is essentially planar (r.m.s. deviation = 0.0104 Å). Intermolecular O—H···Cl and N—H···Cl hydrogen bonds, as well as C—H···O contacts, connect the molecules in the crystal structure. A short C···C distance of only 3.3930 (19) Å between C atoms of neighbouring rings is indicative of π-stacking. The corresponding centroid–centroid distance between the two aromatic systems is 4.2370 (7) Å due to the small overlap of the adjacent rings.

Related literature

For the crystal structure of 3-hydroxy-2-hydroxymethyl-6-methyl-pyridine, see: Casas *et al.* (2007). For graph-set analysis of hydrogen bonds, see: Etter *et al.* (1990); Bernstein *et al.* (1995). For general information about the chelate effect in coordination chemistry, see: Gade (1998).



Experimental

Crystal data

$C_6H_8NO_2^+\cdot Cl^-$
M_r = 161.58
Triclinic, $P\overline{1}$
a = 6.8490 (2) Å
b = 7.1376 (2) Å
c = 7.9675 (2) Å
α = 73.895 (1)°
β = 68.634 (1)°
γ = 86.801 (1)°
V = 348.04 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.48 mm^{-1}
T = 200 K
0.24 × 0.17 × 0.11 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.834, T_{max} = 1.000
6143 measured reflections
1711 independent reflections
1572 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.073
S = 1.06
1711 reflections
103 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H81···Cl1^{i}	0.79 (2)	2.22 (2)	3.0086 (9)	176.1 (19)
O2—H82···Cl1^{ii}	0.85 (2)	2.29 (2)	3.1276 (11)	168.7 (18)
N1—H71···Cl1^{iii}	0.853 (17)	2.391 (17)	3.1739 (10)	152.9 (14)
C3—H3···O2^{iv}	0.95	2.47	3.2069 (14)	134

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y, z$; (iii) $-x+1, -y+2, -z$; (iv) $x, y, z+1$.

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: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

The authors thank Dr James Huddleston for helpful discussions.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FY2019).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2008). *SADABS*. Bruker Inc., Madison, Wisconsin, USA.
Bruker (2010). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Casas, J. S., Castineiras, A., Condori, F., Couce, M. D., Russo, U., Sanchez, A., Sordo, J., Ma Varela, J. & Vazquez Lopez, E. M. (2007). *J. Organomet. Chem.* **692**, 3547–3554.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Gade, L. H. (1998). *Koordinationschemie*, 1. Auflage. Weinheim: Wiley-VCH.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

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S1. Comment

Chelate ligands have found widespread use in coordination chemistry due to the enhanced thermodynamic stability of resultant coordination compounds in relation to coordination compounds exclusively applying comparable monodentate ligands (Gade, 1998). Combining different donor atoms, a molecular set-up to accomodate a large variety of metal centers of variable Lewis acidity is at hand. In this aspect, the title compound seemed of interest due to its possible use as a strictly neutral or, depending on the pH value, as an anionic or cationic ligand. In addition, due to the set-up of its functional groups, it may act as mono- or bidentate ligand offering the possibility to create five- or six-membered chelate rings. To enable comparative studies in terms of bond lengths and angles in the envisioned coordination compounds, we determined the molecular and crystal structure of the title compound. Structural information about 3-hydroxy-2-hydroxy-methyl-6-methyl-pyridine is available in the literature (Casas *et al.*, 2007).

Protonation took place on the nitrogen atom. Intracyclic angles span a range from 118.46 (10) ° to 123.99 (10) ° with the largest angle found on the nitrogen atom and the smallest angle on the carbon atom bearing the hydroxymethyl group. The non-hydrogen atoms of the organic cation essentially lie in one common plane (r.m.s. of fitted non-hydrogen atoms = 0.0104 Å). The hydroxymethyl group adopts a conformation in which the aliphatic hydroxyl group is bent away from the aromatic hydroxyl group (Fig. 1).

In the crystal structure, hydrogen bonds involving all hydroxyl groups and the protonated nitrogen atom as donors are present. In every case, the chloride anion serves as acceptor (Fig. 2). In addition, a C–H···O contact is observed whose range falls by more than 0.2 Å below the sum of van-der-Waals radii of the atoms participating. The latter contact involves the CH group in *ortho* position to the hydroxyl group bound to the aromatic system and the oxygen atom of the aliphatic hyxdroxyl group. A description of the classical hydrogen bonding system in terms of graph-set analysis (Etter *et al.*, 1990; Bernstein *et al.*, 1995) necessitates a *DDD* descriptor on the unitary level while the C–H···O contacts can be described by a *C*(6) descriptor at the same level. A C···C distance of only 3.3930 (19) Å between carbon atoms of neighbouring rings is indicative of π-stacking with the shortest intercentroid distance between two aromatic systems measured at 4.2370 (7) Å due to the small overlap of adjacent rings. In total, the components of the title compound are connected to a three-dimensional network with the C–H···O contacts forming chains along the crystallographic *c* axis.

The packing of the compound in the crystal structure is shown in Figure 3.

S2. Experimental

The compound was obtained commercially (Aldrich). Crystals suitable for the X-ray diffraction study were obtained upon slow evaporation of an aqueous solution of the compound at room temperature.

S3. Refinement

Carbon-bound H atoms were placed in calculated positions (C—H 0.95 Å for aromatic carbon atoms and C—H 0.99 Å for the methylene groups) and were included in the refinement in the riding model approximation, with U(H) set to $1.2U_{eq}$(C). The H atom of the hydroxyl groups as well as the H atom of the protonated nitrogen atom were located on a difference Fourier map and refined with individual thermal parameters.

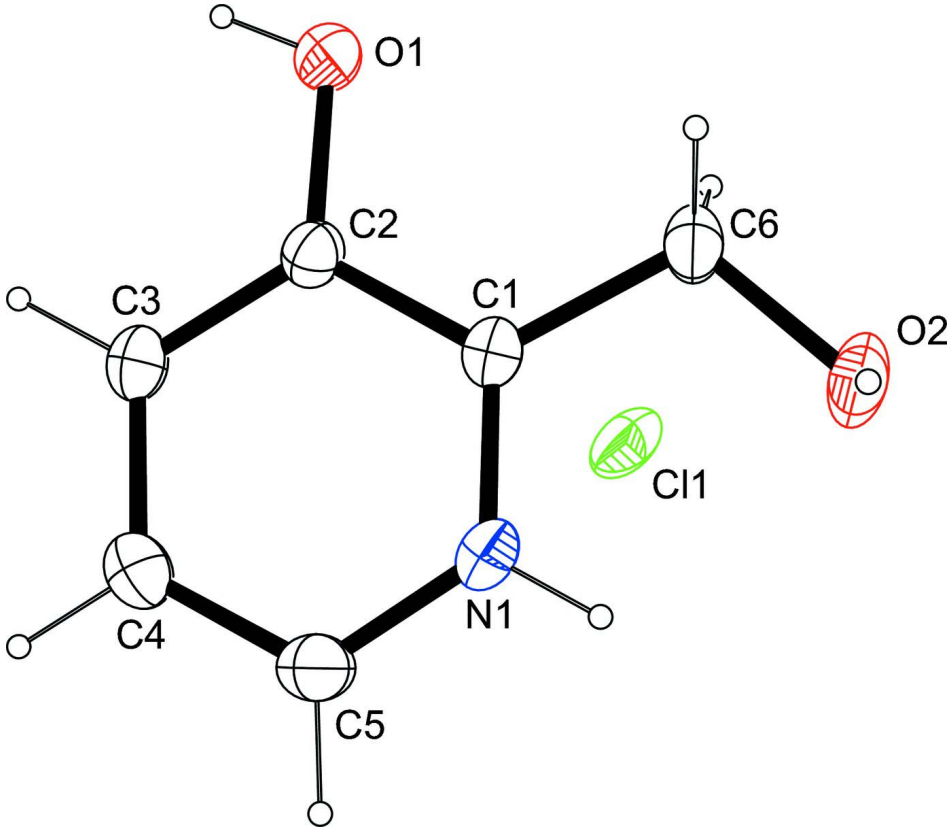

Figure 1

The molecular structure of the title compound, with atom labels and anisotropic displacement ellipsoids (drawn at 50% probability level).

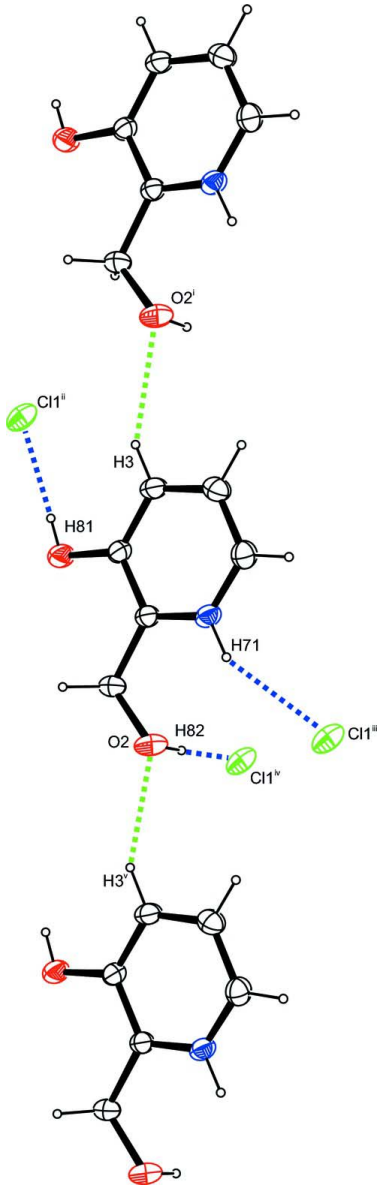

Figure 2

Intermolecular contacts, viewed approximately along [-1 -1 0]. Blue dashed lines indicate classical hydrogen bonds while green dashed lines indicate C–H···O contacts. Symmetry operators: (i) *x*, *y*, *z* + 1; (ii) -*x* + 1, -*y* + 1, -*z* + 1; (iii) -*x* + 1, -*y* + 2, -*z*; (iv) *x* - 1, *y*, *z*; (v) *x*, *y*, *z* - 1.

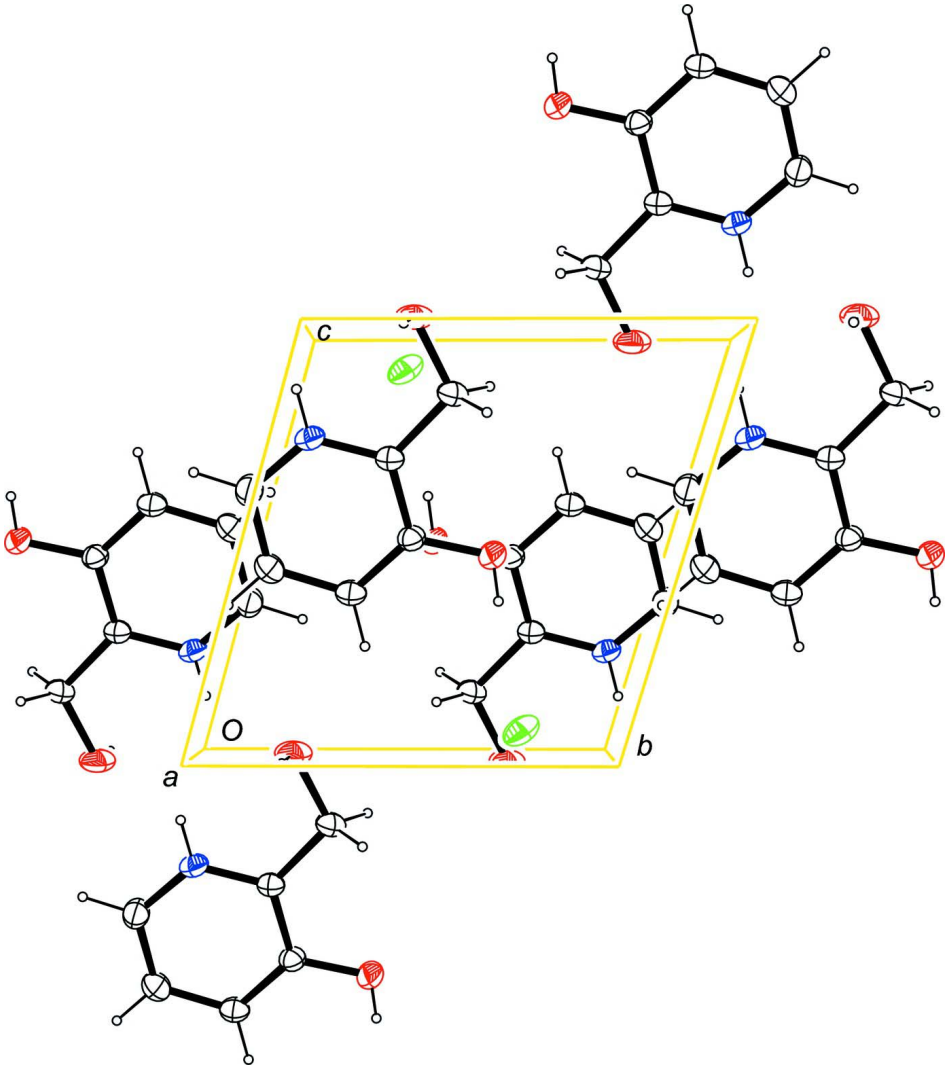

Figure 3

Molecular packing of the title compound, viewed along [-1 0 0] (anisotropic displacement ellipsoids drawn at 50% probability level).

3-Hydroxy-2-(hydroxymethyl)pyridinium chloride

Crystal data

$C_6H_8NO_2^+ \cdot Cl^-$
M_r = 161.58
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 6.8490 (2) Å
b = 7.1376 (2) Å
c = 7.9675 (2) Å
α = 73.895 (1)°
β = 68.634 (1)°
γ = 86.801 (1)°
V = 348.04 (2) Å^3
Z = 2
F(000) = 168
D_x = 1.542 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4561 reflections
θ = 2.9–28.2°
μ = 0.48 mm^{-1}
T = 200 K
Platelet, colourless
0.24 × 0.17 × 0.11 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.834, T_{max} = 1.000
6143 measured reflections
1711 independent reflections
1572 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 28.3°, θ_{min} = 2.9°
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -9 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.073
S = 1.06
1711 reflections
103 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 0.0944P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

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

	x	y	z	U_{iso}*/U_{eq}
O1	0.25186 (15)	0.42693 (12)	0.51787 (12)	0.0286 (2)
H81	0.240 (3)	0.382 (3)	0.624 (3)	0.047 (5)*
O2	0.29516 (16)	0.75828 (14)	−0.01815 (11)	0.0325 (2)
H82	0.166 (3)	0.776 (3)	0.001 (3)	0.051 (5)*
N1	0.27167 (14)	0.91926 (14)	0.25202 (13)	0.0221 (2)
H71	0.276 (2)	0.980 (2)	0.142 (2)	0.035 (4)*
C1	0.26774 (16)	0.72440 (15)	0.29807 (14)	0.0197 (2)
C2	0.25517 (16)	0.62326 (15)	0.47898 (15)	0.0205 (2)
C3	0.24780 (18)	0.72716 (16)	0.60447 (15)	0.0243 (2)
H3	0.2386	0.6601	0.7283	0.029*
C4	0.25391 (18)	0.93031 (17)	0.54794 (16)	0.0263 (2)
H4	0.2494	1.0026	0.6329	0.032*
C5	0.26641 (18)	1.02541 (16)	0.36935 (16)	0.0258 (2)
H5	0.2713	1.1640	0.3288	0.031*
C6	0.28268 (19)	0.62276 (17)	0.15235 (15)	0.0247 (2)
H6A	0.4087	0.5441	0.1314	0.030*
H6B	0.1578	0.5329	0.1981	0.030*
Cl1	0.81001 (5)	0.75715 (4)	0.07668 (4)	0.03225 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0459 (5)	0.0196 (4)	0.0218 (4)	0.0029 (3)	−0.0161 (4)	−0.0034 (3)
O2	0.0412 (5)	0.0395 (5)	0.0163 (4)	0.0019 (4)	−0.0116 (4)	−0.0050 (3)
N1	0.0253 (5)	0.0228 (4)	0.0162 (4)	0.0008 (3)	−0.0081 (3)	−0.0013 (3)

C1	0.0195 (5)	0.0229 (5)	0.0166 (5)	0.0015 (4)	−0.0069 (4)	−0.0049 (4)
C2	0.0221 (5)	0.0210 (5)	0.0183 (5)	0.0018 (4)	−0.0086 (4)	−0.0038 (4)
C3	0.0299 (5)	0.0269 (5)	0.0181 (5)	0.0016 (4)	−0.0118 (4)	−0.0054 (4)
C4	0.0305 (6)	0.0271 (5)	0.0253 (5)	0.0010 (4)	−0.0119 (4)	−0.0111 (4)
C5	0.0292 (5)	0.0202 (5)	0.0279 (6)	0.0005 (4)	−0.0108 (4)	−0.0056 (4)
C6	0.0306 (6)	0.0278 (5)	0.0173 (5)	0.0025 (4)	−0.0096 (4)	−0.0074 (4)
Cl1	0.03770 (18)	0.02940 (16)	0.02636 (16)	−0.00094 (11)	−0.01668 (13)	0.00473 (11)

Geometric parameters (Å, º)

O1—C2	1.3482 (13)	C2—C3	1.3866 (15)
O1—H81	0.79 (2)	C3—C4	1.3921 (16)
O2—C6	1.4085 (13)	C3—H3	0.9500
O2—H82	0.85 (2)	C4—C5	1.3692 (16)
N1—C1	1.3355 (14)	C4—H4	0.9500
N1—C5	1.3470 (15)	C5—H5	0.9500
N1—H71	0.853 (17)	C6—H6A	0.9900
C1—C2	1.3948 (14)	C6—H6B	0.9900
C1—C6	1.5025 (14)		
C2—O1—H81	108.9 (14)	C4—C3—H3	120.2
C6—O2—H82	100.9 (13)	C5—C4—C3	119.70 (10)
C1—N1—C5	123.99 (10)	C5—C4—H4	120.1
C1—N1—H71	118.0 (11)	C3—C4—H4	120.1
C5—N1—H71	118.0 (11)	N1—C5—C4	118.92 (10)
N1—C1—C2	118.46 (10)	N1—C5—H5	120.5
N1—C1—C6	119.00 (9)	C4—C5—H5	120.5
C2—C1—C6	122.52 (10)	O2—C6—C1	111.08 (9)
O1—C2—C3	124.70 (10)	O2—C6—H6A	109.4
O1—C2—C1	115.98 (9)	C1—C6—H6A	109.4
C3—C2—C1	119.32 (10)	O2—C6—H6B	109.4
C2—C3—C4	119.61 (10)	C1—C6—H6B	109.4
C2—C3—H3	120.2	H6A—C6—H6B	108.0
C5—N1—C1—C2	0.71 (16)	C1—C2—C3—C4	−0.27 (17)
C5—N1—C1—C6	−177.70 (10)	C2—C3—C4—C5	0.23 (18)
N1—C1—C2—O1	−179.96 (9)	C1—N1—C5—C4	−0.76 (17)
C6—C1—C2—O1	−1.61 (15)	C3—C4—C5—N1	0.26 (17)
N1—C1—C2—C3	−0.18 (15)	N1—C1—C6—O2	−1.18 (14)
C6—C1—C2—C3	178.17 (10)	C2—C1—C6—O2	−179.52 (10)
O1—C2—C3—C4	179.49 (11)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H81···Cl1^{i}	0.79 (2)	2.22 (2)	3.0086 (9)	176.1 (19)
O2—H82···Cl1^{ii}	0.85 (2)	2.29 (2)	3.1276 (11)	168.7 (18)

N1—H71···Cl1^{iii}	0.853 (17)	2.391 (17)	3.1739 (10)	152.9 (14)
C3—H3···O2^{iv}	0.95	2.47	3.2069 (14)	134

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y, z$; (iii) $-x+1, -y+2, -z$; (iv) $x, y, z+1$.