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Crystal structure of 2-methyl-1*H*-imidazol-3-ium hydrogen oxalate dihydrate

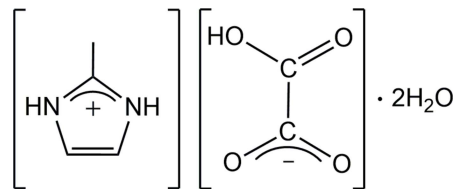
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Single crystals of the title molecular salt, C₄H₇N₂⁺·HC₂O₄⁻·2H₂O, were isolated from the reaction of 2-methyl-1*H*-imidazole and oxalic acid in a 1:1 molar ratio in water. In the crystal, the cations and anions are positioned alternately along an infinite [010] ribbon and linked together through bifurcated N—H···(O,O) hydrogen bonds. The water molecules of crystallization link the chains into (10 ) bilayers, with the methyl groups of the cations organized in an isotactic manner.

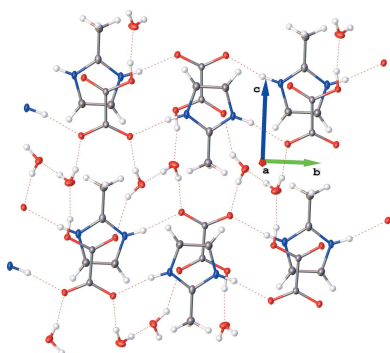
1. Chemical context

Imidazolium-type building blocks are useful in the field of crystal engineering (MacDonald *et al.*, 2001). With many possibilities of substitution (involving various positions around the five-membered ring) and *via* the propagation of multidirectional hydrogen-bonding interactions, they easily lead to the self-assembly of poly-dimensional packing networks. In 2010, Callear and co-workers described various topologies based on imidazolium/dicarboxylic acid combinations and showed the crystal-packing effects of substitution in the imidazole ring (Callear *et al.*, 2010). In this context, and for some time, our group has focused on the contribution of the 2-methylimidazolium cation as a co-crystal in organic (Diop, Diop & Maris, 2016) and organic–inorganic hybrid salts (Diop, Diop & Maris, 2015; Diop, Diop, Plasseraud & Maris, 2015, 2016). Continuing our ongoing studies in this field, we report herein the crystal structure of a new hydrated organic salt, namely 2-methyl-1*H*-imidazol-3-ium hydrogen oxalate dihydrate, (I), isolated by reacting 2-methyl-1*H*-imidazole and oxalic acid in a 1:1 molar ratio in water.



2. Structural comments

The asymmetric unit of the title molecular salt (I) consists of four components, *i.e.* one 2-methyl-1*H*-imidazol-3-ium cation, one hydrogen oxalate anion and two solvent water molecules (Fig. 1). The hydrogen oxalate anion is slightly twisted, with O1—C6—C5—O3 and O2—C6—C5—O4 torsion angles of



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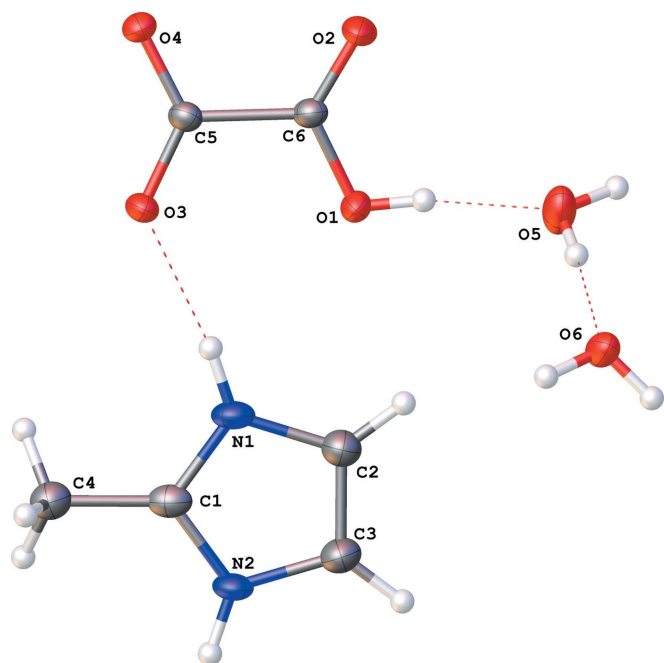


Figure 1
The molecular structure of (I), showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

6.9 (3) and 7.3 (3)°, respectively. The C5–O3 and C5–O4 bonds are almost equal in length [1.249 (2) and 1.245 (2) Å, respectively], whereas C6–O2 is typical for a >C=O group [1.206 (2) Å] and C6–O1 has a normal C–OH bond length [1.306 (2) Å] (Adams, 1978).

3. Supramolecular features

Hydrogen-bonding interactions are listed in Table 1 and illustrated in Fig. 2. Both N–H groups of the imidazolium cation are involved in asymmetric bifurcated N–H···(O,O) hydrogen bonds with two distinct neighbouring hydrogen oxalate anions, which initiates the propagation of an infinite ribbon along the *b*-axis direction. Considering the orientation of the methyl groups of the cations along the ribbon, the sequence can be described as ‘isotactic’. The cations and anions are positioned alternately and are almost coplanar [dihedral angle between adjacent species = 1.15 (9)°].

As well as the cation-to-anion links, the OH group of the anion acts as a hydrogen-bond donor with one molecule of water, which is also the donor for hydrogen-bond interactions with (i) a second molecule of water and (ii) an O atom of a hydrogen oxalate anion involved in a neighbouring ribbon. The second water molecule also bridges two distinct hydrogen oxalate anions through two O–H···O hydrogen bonds. Thus, all the O atoms of the hydrogen oxalate anions are involved in the hydrogen-bonding network.

The supramolecular arrangement depicted in Fig. 2 relies on the contributions of the four components of (I) and can be described as resulting from three levels of organization: (i) C₄H₇N₂⁺ and HC₂O₄[−] assembled in infinite ribbons; (ii) parallel ribbons of C₄H₇N₂⁺/HC₂O₄[−] connected together by

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1···O3	0.88	1.94	2.811 (2)	172
N1–H1···O1	0.88	2.50	2.991 (2)	116
N2–H2···O4 ⁱ	0.88	1.97	2.842 (2)	169
N2–H2···O2 ⁱ	0.88	2.49	2.977 (2)	116
O1–H1A···O5	0.84	1.69	2.5234 (19)	169
O6–H6A···O2 ⁱⁱ	0.85	2.02	2.7893 (19)	150
O6–H6B···O3 ⁱⁱⁱ	0.85	1.87	2.700 (2)	166
O5–H5A···O6	0.85	1.82	2.672 (2)	176
O5–H5B···O4 ^{iv}	0.85	1.88	2.720 (2)	167

Symmetry codes: (i) $x, y - 1, z$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$.

water molecules, which leads to a staircase–sheet structure; (iii) sheets stacked in pairs which can be described as a two-dimensional bilayer-like arrangement propagating in (10 $\bar{1}$). This final organization is again induced by the formation of hydrogen-bonding interactions between the water molecules contained in each sheet. The inter-sheet distance is about 3.4 Å. Interestingly, all the methyl substituents of the imidazolium rings are oriented in the same direction along the *c* axis. Thus, the isotacticity observed at the ribbon level is also extended across the supramolecular network.

4. Database survey

To date, 176 structures of hydrogen oxalates have been deposited in the Cambridge Structural Database (CSD; Groom *et al.*, 2016). Among these, five hits describe imidazolium salts or derivatives, *i.e.* imidazolium hydrogen oxalate

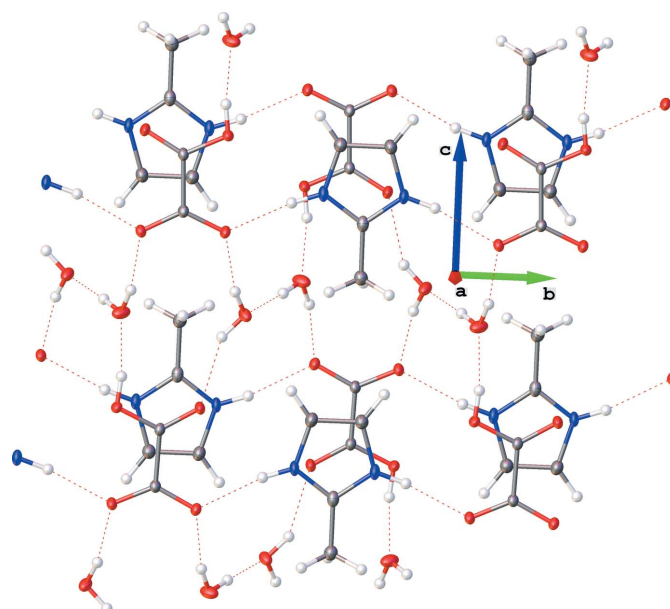


Figure 2
The crystal packing of the title salt, showing a two-dimensional bilayer-like arrangement through N–H···(O,O) and O–H···O interactions. H atoms not involved in hydrogen bonding have been omitted for clarity. Colour code: C dark grey, H light grey, O red and N blue.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₄ H ₇ N ₂ ⁺ ·C ₂ HO ₄ ⁻ ·2H ₂ O
<i>M_r</i>	208.18
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	115
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.7139 (7), 9.5116 (7), 15.2115 (13)
β (°)	101.151 (6)
<i>V</i> (Å ³)	953.07 (15)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.13
Crystal size (mm)	0.30 × 0.10 × 0.08
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2014)
<i>T</i> _{min} – <i>T</i> _{max}	0.691, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	15445, 2187, 1258
<i>R</i> _{int}	0.063
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.650
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.043, 0.115, 1.01
No. of reflections	2187
No. of parameters	135
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.40, -0.23

Computer programs: *APEX2* and *SAINTE* (Bruker, 2013), *SHELXS2013* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

[CSD refcodes MEQPAZ (MacDonald *et al.*, 2001) and MEQPAZ01 (Prasad *et al.*, 2002)], (*S*)-(+)-2-[2-(biphenyl-2-yl)-1-methylethyl]-4,5-dihydro-1*H*-imidazolium hydrogen oxalate (GAQTOI; Giannella *et al.*, 2005), 1,3-diisopropyl-4,5-dimethylimidazolium hydrogen oxalate (DOHTOK; Abu-Rayyan *et al.*, 2008), (*S*)-(–)-6-(4-bromophenyl)-2,3,5,6-tetrahydrothiazolo[2,3-*b*]imidazolium hydrogen oxalate (ROFQAF; Minor & Chruszcz, 2008).

5. Synthesis and crystallization

Equimolar solutions of 2-methyl-1*H*-imidazole (6.51 g, 79.39 mmol) and H₂C₂O₄·2H₂O (10.00 g, 79.39 mmol) in water (100 ml) were mixed together at room temperature (301 K). Needle-shaped colourless crystals of (**I**) were obtained after one week by evaporation of the solvent at 333 K (yield 10.83 g, 65.5%).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms on C, O and N atoms were placed at calculated positions using a riding model, with aromatic C–H = 0.95 Å and aromatic N–H = 0.88 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(C,N), or hydroxy O–H = 0.84 Å, water O–H = 0.85 Å and methyl C–H = 0.98 Å, and with *U*_{iso}(H) = 1.5*U*_{eq}(O,C).

Acknowledgements

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Crystal structure of 2-methyl-1*H*-imidazol-3-ium hydrogen oxalate dihydrate

Mouhamadou Birame Diop, Libasse Diop, Laurent Plasseraud and H el ene Cattey

Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

2-Methyl-1*H*-imidazol-3-ium hydrogen oxalate dihydrate

Crystal data

$C_4H_7N_2^+ \cdot C_2HO_4^- \cdot 2H_2O$

$M_r = 208.18$

Monoclinic, $P2_1/n$

$a = 6.7139$ (7)  

$b = 9.5116$ (7)  

$c = 15.2115$ (13)  

$\beta = 101.151$ (6) 

$V = 953.07$ (15)  ³

$Z = 4$

$F(000) = 440$

$D_x = 1.451$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$  

Cell parameters from 2578 reflections

$\theta = 3.5\text{--}26.4^\circ$

$\mu = 0.13$ mm⁻¹

$T = 115$ K

Needle, colourless

$0.30 \times 0.10 \times 0.08$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: X-ray tube, Siemens KFF Mo
2K-90C

TRIUMPH curved crystal monochromator

Detector resolution: 1024 x 1024 pixels mm⁻¹

φ and ω scans'

Absorption correction: multi-scan

SADABS (Bruker, 2014) was used for

absorption correction. $wR2(\text{int})$ was 0.0622

before and 0.0548 after correction. The Ratio of
minimum to maximum transmission is 0.9269.

The $\lambda/2$ correction factor is 0.00150.

$T_{\min} = 0.691$, $T_{\max} = 0.746$

15445 measured reflections

2187 independent reflections

1258 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.063$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -8 \rightarrow 8$

$k = -12 \rightarrow 12$

$l = -19 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.115$

$S = 1.01$

2187 reflections

135 parameters

0 restraints

Hydrogen site location: mixed

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.3824P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$$

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O4	0.3344 (2)	0.84241 (13)	0.62704 (8)	0.0224 (3)
O3	0.3377 (2)	0.60714 (13)	0.62300 (9)	0.0247 (3)
O1	0.1928 (2)	0.60978 (13)	0.44891 (9)	0.0254 (4)
H1A	0.1572	0.6196	0.3932	0.038*
O6	0.3979 (2)	0.45757 (14)	0.22494 (10)	0.0314 (4)
H6A	0.3724	0.3954	0.1842	0.047*
H6B	0.4883	0.4270	0.2677	0.047*
O2	0.2253 (2)	0.84212 (14)	0.44546 (9)	0.0311 (4)
O5	0.1121 (3)	0.61142 (17)	0.27986 (9)	0.0357 (4)
H5A	0.1986	0.5615	0.2599	0.054*
H5B	0.0183	0.6360	0.2367	0.054*
N2	0.2719 (2)	0.11229 (16)	0.54620 (11)	0.0231 (4)
H2	0.2824	0.0244	0.5647	0.028*
N1	0.2803 (2)	0.33729 (17)	0.54697 (11)	0.0245 (4)
H1	0.2970	0.4248	0.5657	0.029*
C5	0.3089 (3)	0.7264 (2)	0.58854 (12)	0.0186 (4)
C6	0.2361 (3)	0.7327 (2)	0.48607 (12)	0.0187 (4)
C1	0.3139 (3)	0.2239 (2)	0.59833 (14)	0.0244 (5)
C2	0.2138 (3)	0.2951 (2)	0.45809 (14)	0.0287 (5)
H2A	0.1789	0.3549	0.4074	0.034*
C4	0.3880 (3)	0.2233 (2)	0.69571 (13)	0.0291 (5)
H4A	0.3300	0.1428	0.7222	0.044*
H4B	0.3472	0.3106	0.7215	0.044*
H4C	0.5364	0.2160	0.7085	0.044*
C3	0.2088 (3)	0.1547 (2)	0.45810 (14)	0.0296 (5)
H3	0.1696	0.0954	0.4075	0.036*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O4	0.0311 (8)	0.0146 (7)	0.0198 (7)	-0.0010 (6)	0.0005 (6)	-0.0023 (6)
O3	0.0375 (9)	0.0141 (7)	0.0196 (7)	0.0018 (6)	-0.0018 (6)	0.0018 (6)
O1	0.0417 (10)	0.0159 (7)	0.0160 (7)	-0.0014 (6)	-0.0010 (7)	-0.0013 (5)
O6	0.0439 (11)	0.0223 (8)	0.0224 (8)	0.0083 (7)	-0.0075 (7)	-0.0045 (6)
O2	0.0568 (11)	0.0135 (7)	0.0203 (8)	-0.0004 (7)	0.0009 (7)	0.0024 (6)
O5	0.0412 (11)	0.0421 (10)	0.0201 (8)	0.0125 (8)	-0.0030 (7)	-0.0046 (7)

N2	0.0282 (10)	0.0116 (8)	0.0285 (10)	-0.0004 (7)	0.0026 (8)	0.0012 (7)
N1	0.0280 (10)	0.0128 (8)	0.0322 (10)	0.0004 (7)	0.0043 (8)	-0.0006 (7)
C5	0.0192 (11)	0.0153 (9)	0.0200 (10)	0.0020 (8)	0.0010 (8)	0.0006 (8)
C6	0.0198 (10)	0.0145 (9)	0.0209 (10)	0.0008 (8)	0.0016 (8)	-0.0011 (8)
C1	0.0218 (11)	0.0178 (9)	0.0332 (12)	0.0000 (9)	0.0047 (9)	-0.0005 (9)
C2	0.0363 (13)	0.0221 (11)	0.0265 (11)	0.0009 (10)	0.0029 (10)	0.0007 (9)
C4	0.0348 (13)	0.0238 (10)	0.0282 (11)	-0.0002 (10)	0.0053 (10)	-0.0016 (9)
C3	0.0395 (14)	0.0205 (11)	0.0276 (12)	-0.0001 (10)	0.0033 (10)	-0.0028 (9)

Geometric parameters (Å, °)

O4—C5	1.245 (2)	N1—H1	0.8800
O3—C5	1.249 (2)	N1—C1	1.325 (3)
O1—H1A	0.8400	N1—C2	1.398 (2)
O1—C6	1.306 (2)	C5—C6	1.542 (3)
O6—H6A	0.8499	C1—C4	1.469 (3)
O6—H6B	0.8501	C2—H2A	0.9500
O2—C6	1.206 (2)	C2—C3	1.336 (3)
O5—H5A	0.8500	C4—H4A	0.9800
O5—H5B	0.8500	C4—H4B	0.9800
N2—H2	0.8800	C4—H4C	0.9800
N2—C1	1.323 (2)	C3—H3	0.9500
N2—C3	1.385 (2)		
C6—O1—H1A	109.5	N2—C1—N1	107.91 (17)
H6A—O6—H6B	109.5	N2—C1—C4	126.36 (18)
H5A—O5—H5B	109.5	N1—C1—C4	125.72 (18)
C1—N2—H2	125.2	N1—C2—H2A	126.6
C1—N2—C3	109.64 (16)	C3—C2—N1	106.85 (18)
C3—N2—H2	125.2	C3—C2—H2A	126.6
C1—N1—H1	125.6	C1—C4—H4A	109.5
C1—N1—C2	108.83 (16)	C1—C4—H4B	109.5
C2—N1—H1	125.6	C1—C4—H4C	109.5
O4—C5—O3	127.68 (17)	H4A—C4—H4B	109.5
O4—C5—C6	115.41 (16)	H4A—C4—H4C	109.5
O3—C5—C6	116.90 (17)	H4B—C4—H4C	109.5
O1—C6—C5	113.79 (16)	N2—C3—H3	126.6
O2—C6—O1	124.38 (17)	C2—C3—N2	106.76 (18)
O2—C6—C5	121.81 (18)	C2—C3—H3	126.6
O4—C5—C6—O1	-173.95 (17)	C1—N1—C2—C3	0.0 (2)
O4—C5—C6—O2	7.3 (3)	C2—N1—C1—N2	0.0 (2)
O3—C5—C6—O1	6.9 (3)	C2—N1—C1—C4	179.0 (2)
O3—C5—C6—O2	-171.78 (19)	C3—N2—C1—N1	0.0 (2)
N1—C2—C3—N2	0.0 (2)	C3—N2—C1—C4	-179.1 (2)
C1—N2—C3—C2	0.0 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1···O3	0.88	1.94	2.811 (2)	172
N1—H1···O1	0.88	2.50	2.991 (2)	116
N2—H2···O4 ⁱ	0.88	1.97	2.842 (2)	169
N2—H2···O2 ⁱ	0.88	2.49	2.977 (2)	116
O1—H1A···O5	0.84	1.69	2.5234 (19)	169
O6—H6A···O2 ⁱⁱ	0.85	2.02	2.7893 (19)	150
O6—H6B···O3 ⁱⁱⁱ	0.85	1.87	2.700 (2)	166
O5—H5A···O6	0.85	1.82	2.672 (2)	176
O5—H5B···O4 ^{iv}	0.85	1.88	2.720 (2)	167

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1/2, y-1/2, -z+1/2$; (iii) $-x+1, -y+1, -z+1$; (iv) $x-1/2, -y+3/2, z-1/2$.