

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

**( $\mu$ -Dihydrogen pyrazine-2,3,5,6-tetracarboxylato- $\kappa^6O^2,N^1,O^6;O^3,N^4,O^5$ )bis-(diaqualithium) monohydrate**

Wojciech Starosta and Janusz Leciejewicz\*

Institute of Nuclear Chemistry and Technology, ul.Dorodna 16, 03-195 Warszawa, Poland

Correspondence e-mail: j.leciejewicz@ichtj.waw.pl

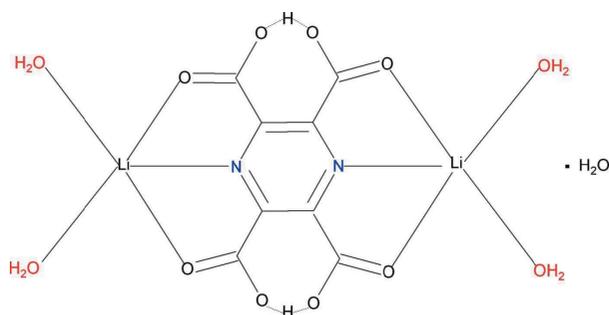
Received 17 March 2014; accepted 1 April 2014

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(C-C) = 0.002$  Å;  $R$  factor = 0.047;  $wR$  factor = 0.100; data-to-parameter ratio = 11.8.

The structure of the title compound,  $[Li_2(C_8H_2N_2O_8)(H_2O)_4] \cdot H_2O$ , is composed of dinuclear molecules in which the ligand bridges two symmetry-related  $Li^I$  ions, each coordinated also by two water O atoms, in an  $O,N,O'$ -manner. The Li and N atoms occupy special positions on twofold rotation axes, whereas a crystal water molecule is located at the intersection of three twofold rotation axes. The  $Li^I$  cation shows a distorted trigonal-bipyramidal coordination. Two carboxylate groups remain protonated and form short interligand hydrogen bonds. The molecules are held together by a network of hydrogen bonds in which the coordinating and solvation water molecules act as donors and carboxylate O atoms as acceptors, forming a three-dimensional architecture.

## Related literature

For the structure of a lithium complex with pyrazine-2,3,5,6-tetracarboxylate and water ligands, see: Starosta & Leciejewicz (2010). The structure of pyrazine-2,3,5,6-tetracarboxylic acid dihydrate was reported by Vishweshwar *et al.* (2001).



## Experimental

## Crystal data

$[Li_2(C_8H_2N_2O_8)(H_2O)_4] \cdot H_2O$   
 $M_r = 358.08$   
 Orthorhombic, *Ibam*  
 $a = 6.3807$  (4) Å  
 $b = 9.8331$  (6) Å  
 $c = 22.1717$  (16) Å

$V = 1391.10$  (16) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.16$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.12 \times 0.10 \times 0.06$  mm

## Data collection

Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer  
 Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)  
 $T_{min} = 0.979$ ,  $T_{max} = 0.993$

3622 measured reflections  
 917 independent reflections  
 769 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.061$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.100$   
 $S = 1.06$   
 917 reflections  
 78 parameters  
 4 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{max} = 0.25$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.22$  e Å<sup>-3</sup>

Table 1

Selected bond lengths (Å).

|        |             |                     |             |
|--------|-------------|---------------------|-------------|
| Li1–N1 | 2.053 (4)   | Li1–O3 <sup>i</sup> | 1.969 (3)   |
| Li1–O1 | 2.1581 (17) | Li1–O1 <sup>i</sup> | 2.1580 (17) |
| Li1–O3 | 1.969 (3)   |                     |             |

Symmetry code: (i)  $-x + 2, -y, z$ .

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$                           | $D-H$    | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|--|----------|--------------|--------------|----------------|
| O2–H1 <sup>i</sup> ···O2 <sup>ii</sup>   | 1.20 (1) | 1.20 (1)     | 2.402 (3)    | 177 (8)        |
| O3–H32 <sup>i</sup> ···O3 <sup>iii</sup> | 0.87 (2) | 2.00 (2)     | 2.839 (3)    | 163 (4)        |
| O3–H31 <sup>i</sup> ···O1 <sup>iv</sup>  | 0.86 (2) | 2.03 (2)     | 2.8825 (19)  | 177 (2)        |
| O3–H33 <sup>i</sup> ···O4 <sup>v</sup>   | 0.86 (2) | 2.10 (2)     | 2.9454 (17)  | 169 (6)        |

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

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supporting information for this paper is available from the IUCr electronic archives (Reference: KP2468).

## References

- Agilent (2011). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Starosta, W. & Leciejewicz, J. (2010). *Acta Cryst.* **E66**, m1561–m1562.  
 Vishweshwar, P., Nangia, A. & Lynch, V. M. (2001). *Chem. Commun.* pp. 179–180.

## supporting information

*Acta Cryst.* (2014). E70, m172 [doi:10.1107/S1600536814007223]

**( $\mu$ -Dihydrogen pyrazine-2,3,5,6-tetracarboxylato- $\kappa^6O^2,N^1,O^6;O^3,N^4,O^5$ )bis(di-aqualithium) monohydrate**

**Wojciech Starosta and Janusz Leciejewicz**

### S1. Comment

The structure of the title compound reveals a dimeric unit of  $2/m$  crystallographic symmetry in which two symmetry related doubly aqua-coordinated Li(I) ions are bridged by a ligand molecule *via* its both N,*O,O* bonding sites (Fig.1). The Li(I) cation is in distorted trigonal bipyramidal coordination. Its equatorial plane is formed by N1, O3, O3<sup>(i)</sup> and the Li1 atoms; the O1 and O1<sup>(i)</sup> atoms are at the apices. The O1—Li—O1<sup>(i)</sup> angle is 151.7 (3)° and Li—O and Li—N bond distances are listed in Table 1. The pyrazine ring is planar. Two carboxylate groups remain protonated to maintain charge balance. Bond distances and bond angles within the hetero-ring do not differ from those reported in the structure of the parent acid (Vishweshwar *et al.*, 2001). Short, symmetric hydrogen bond is formed in which the carboxylate O2 atom is as a donor and the O1<sup>(ii)</sup> is as an acceptor (Table 2). A dihedral angle formed with the pyrazine ring by the carboxylic group C1/O1/O2 is 4.7 (1)°. Fourier maps show a clear disorder in hydrogen positions at the solvation and coordinated water molecules with position occupancy of approximately 0.5. The title molecules are held together by a network of hydrogen bonds (Table 2) in which coordinated water molecules act as donors and carboxylate O atoms as acceptors forming molecular layers propagating in the crystal *a* direction (Fig.2). A view of a single layer is displayed in Fig. 2. The layers are linked by weak hydrogen bonds in which solvation water molecules are involved. Another Li(I) complex with the title ligand is known (Starosta & Leciejewicz, 2010). Its polarized dinuclear structural unit is built of a doubly protonated ligand molecule chelated by its N,*O,O* bonding moiety to an Li(I) ion and an Li(I) ion coordinated by four aqua O atoms. Two of the latter bridge the Li ions to form a catenated polymeric structure propagating in the crystal *a* direction.

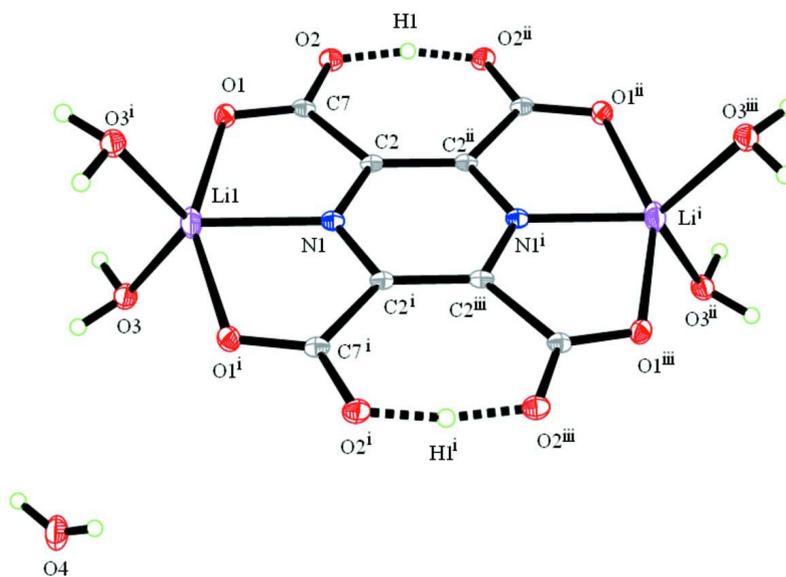
### S2. Experimental

Hot aqueous solutions, one containing 1 mmol of pyrazine-2,3,5,6-tetracarboxylic acid dihydrate, the other 4 mmol of lithium nitrate (Aldrich) were mixed and boiled under reflux with constant stirring for 6 h. After cooling to room temperature the solution was left to evaporate. A couple of days later, single-crystal blocks deposited on the bottom of a crystallization pot. They were washed with cold ethanol and dried in air.

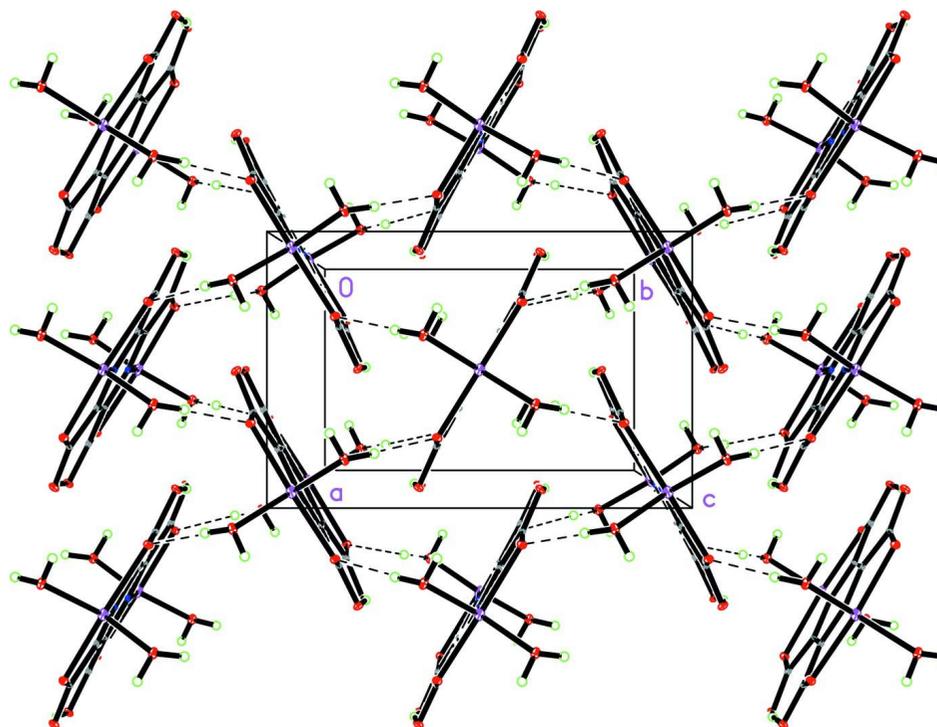
### S3. Refinement

Water and carboxylate H atoms were found in the Fourier map and refined isotropically.

i

**Figure 1**

The molecule of the title compound with atom labelling scheme and 50% probability displacement ellipsoids. Symmetry code: <sup>i</sup>  $-x, -y, z$ ; <sup>ii</sup>  $x, y, -z$ ; <sup>iii</sup>  $-x, -y, -z$ .

**Figure 2**

A single molecular layer composed of the dimers linked by a hydrogen bond network as viewed along the crystal *c* direction.

**( $\mu$ -Dihydrogen pyrazine-2,3,5,6-tetracarboxylato- $\kappa^6O^2,N^1,O^6;O^3,N^4,O^5$ )bis(diaqualithium) monohydrate***Crystal data*[Li<sub>2</sub>(C<sub>8</sub>H<sub>2</sub>N<sub>2</sub>O<sub>8</sub>)(H<sub>2</sub>O)<sub>4</sub>] $\cdot$ H<sub>2</sub>O $M_r = 358.08$ Orthorhombic, *Ibam*

Hall symbol: -I 2 2c

 $a = 6.3807$  (4) Å $b = 9.8331$  (6) Å $c = 22.1717$  (16) Å $V = 1391.10$  (16) Å<sup>3</sup> $Z = 4$  $F(000) = 736$  $D_x = 1.710$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å $\mu = 0.16$  mm<sup>-1</sup> $T = 293$  K

Plate, colourless

0.12  $\times$  0.10  $\times$  0.06 mm*Data collection*

Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer

Radiation source: SuperNova (Mo) X-ray Source

Mirror monochromator

Detector resolution: 16.0131 pixels mm<sup>-1</sup> $\omega$  scansAbsorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011) $T_{\min} = 0.979$ ,  $T_{\max} = 0.993$ 

3622 measured reflections

917 independent reflections

769 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.061$  $\theta_{\max} = 29.3^\circ$ ,  $\theta_{\min} = 3.7^\circ$  $h = -8 \rightarrow 8$  $k = -12 \rightarrow 13$  $l = -29 \rightarrow 29$ *Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.047$  $wR(F^2) = 0.100$  $S = 1.06$ 

917 reflections

78 parameters

4 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

 $w = 1/[\sigma^2(F_o^2) + (0.024P)^2 + 2.020P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} < 0.001$  $\Delta\rho_{\max} = 0.25$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.22$  e Å<sup>-3</sup>*Special details*

**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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)*

|    | $x$        | $y$          | $z$         | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|----|------------|--------------|-------------|----------------------------------|-----------|
| N1 | 1.0000     | 0.0000       | 0.06097 (8) | 0.0207 (4)                       |           |
| O1 | 0.7218 (2) | 0.11263 (14) | 0.12977 (5) | 0.0328 (3)                       |           |
| O3 | 1.1372 (3) | 0.14626 (15) | 0.19959 (7) | 0.0376 (4)                       |           |
| O2 | 0.5112 (3) | 0.16787 (13) | 0.05418 (6) | 0.0356 (4)                       |           |

|     |            |              |              |             |      |
|-----|------------|--------------|--------------|-------------|------|
| C2  | 0.8398 (3) | 0.05696 (15) | 0.03197 (7)  | 0.0203 (3)  |      |
| C7  | 0.6800 (3) | 0.11721 (16) | 0.07586 (8)  | 0.0251 (4)  |      |
| Li1 | 1.0000     | 0.0000       | 0.15359 (19) | 0.0360 (10) |      |
| O4  | 0.0000     | 0.5000       | 0.2500       | 0.0595 (9)  |      |
| H31 | 1.158 (4)  | 0.219 (2)    | 0.1789 (10)  | 0.056 (8)*  |      |
| H1  | 0.506 (12) | 0.168 (4)    | 0.0000       | 0.097 (15)* |      |
| H32 | 1.068 (6)  | 0.161 (4)    | 0.2328 (13)  | 0.037 (13)* | 0.50 |
| H41 | 0.043 (12) | 0.459 (6)    | 0.2190 (17)  | 0.10 (3)*   | 0.50 |
| H33 | 1.254 (6)  | 0.111 (6)    | 0.211 (2)    | 0.08 (2)*   | 0.50 |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$   | $U^{22}$   | $U^{33}$    | $U^{12}$    | $U^{13}$    | $U^{23}$    |
|-----|------------|------------|-------------|-------------|-------------|-------------|
| N1  | 0.0218 (8) | 0.0189 (8) | 0.0214 (9)  | 0.0016 (8)  | 0.000       | 0.000       |
| O1  | 0.0355 (7) | 0.0383 (7) | 0.0244 (6)  | 0.0065 (6)  | 0.0072 (6)  | -0.0025 (5) |
| O3  | 0.0474 (9) | 0.0347 (8) | 0.0308 (8)  | -0.0074 (7) | -0.0008 (7) | 0.0004 (6)  |
| O2  | 0.0293 (7) | 0.0400 (7) | 0.0376 (7)  | 0.0154 (6)  | 0.0050 (7)  | 0.0002 (6)  |
| C2  | 0.0198 (8) | 0.0174 (7) | 0.0239 (8)  | 0.0002 (6)  | 0.0008 (6)  | -0.0009 (6) |
| C7  | 0.0258 (8) | 0.0203 (7) | 0.0293 (9)  | 0.0019 (6)  | 0.0047 (7)  | -0.0008 (6) |
| Li1 | 0.046 (2)  | 0.039 (2)  | 0.024 (2)   | -0.005 (2)  | 0.000       | 0.000       |
| O4  | 0.076 (3)  | 0.065 (2)  | 0.0372 (19) | 0.000       | 0.000       | 0.000       |

*Geometric parameters (Å, °)*

|                         |             |                                      |             |
|-------------------------|-------------|--------------------------------------|-------------|
| N1—C2 <sup>i</sup>      | 1.3313 (18) | O2—C7                                | 1.280 (2)   |
| N1—C2                   | 1.3313 (18) | O2—H1                                | 1.202 (3)   |
| Li1—N1                  | 2.053 (4)   | C2—C2 <sup>ii</sup>                  | 1.418 (3)   |
| O1—C7                   | 1.226 (2)   | C2—C7                                | 1.529 (2)   |
| Li1—O1                  | 2.1581 (17) | Li1—O3 <sup>i</sup>                  | 1.969 (3)   |
| Li1—O3                  | 1.969 (3)   | Li1—O1 <sup>i</sup>                  | 2.1580 (17) |
| O3—H31                  | 0.858 (16)  | Li1—H33                              | 2.33 (5)    |
| O3—H32                  | 0.870 (19)  | O4—H41                               | 0.84 (2)    |
| O3—H33                  | 0.86 (2)    |                                      |             |
| C2 <sup>i</sup> —N1—C2  | 122.24 (19) | O2—C7—C2                             | 118.22 (15) |
| C2 <sup>i</sup> —N1—Li1 | 118.88 (10) | O3 <sup>i</sup> —Li1—O3              | 117.6 (2)   |
| C2—N1—Li1               | 118.88 (10) | O3 <sup>i</sup> —Li1—N1              | 121.21 (11) |
| C7—O1—Li1               | 115.89 (16) | O3—Li1—N1                            | 121.21 (11) |
| Li1—O3—H31              | 113.4 (17)  | O3 <sup>i</sup> —Li1—O1 <sup>i</sup> | 96.76 (7)   |
| Li1—O3—H32              | 110 (3)     | O3—Li1—O1 <sup>i</sup>               | 97.81 (7)   |
| H31—O3—H32              | 113 (3)     | N1—Li1—O1 <sup>i</sup>               | 75.84 (11)  |
| Li1—O3—H33              | 104 (4)     | O3 <sup>i</sup> —Li1—O1              | 97.81 (7)   |
| H31—O3—H33              | 111 (4)     | O3—Li1—O1                            | 96.76 (7)   |
| H32—O3—H33              | 105 (4)     | N1—Li1—O1                            | 75.84 (11)  |
| C7—O2—H1                | 113 (4)     | O1 <sup>i</sup> —Li1—O1              | 151.7 (2)   |
| N1—C2—C2 <sup>ii</sup>  | 118.88 (10) | O3 <sup>i</sup> —Li1—H33             | 111.5 (14)  |
| N1—C2—C7                | 111.58 (14) | O3—Li1—H33                           | 20.9 (10)   |
| C2 <sup>ii</sup> —C2—C7 | 129.53 (9)  | N1—Li1—H33                           | 123.2 (14)  |

|          |             |                          |            |
|----------|-------------|--------------------------|------------|
| O1—C7—O2 | 124.31 (16) | O1 <sup>i</sup> —Li1—H33 | 78.6 (10)  |
| O1—C7—C2 | 117.47 (16) | O1—Li1—H33               | 117.7 (10) |

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

*Hydrogen-bond geometry (Å, °)*

| <i>D—H...A</i>             | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|----------------------------|------------|--------------|--------------|----------------|
| O2—H1...O2 <sup>ii</sup>   | 1.20 (1)   | 1.20 (1)     | 2.402 (3)    | 177 (8)        |
| O3—H32...O3 <sup>iii</sup> | 0.87 (2)   | 2.00 (2)     | 2.839 (3)    | 163 (4)        |
| O3—H31...O1 <sup>iv</sup>  | 0.86 (2)   | 2.03 (2)     | 2.8825 (19)  | 177 (2)        |
| O3—H33...O4 <sup>v</sup>   | 0.86 (2)   | 2.10 (2)     | 2.9454 (17)  | 169 (6)        |

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