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Redetermination of the crystal structure of 2-oxo-1,3-thiazolidin-4-iminium chloride

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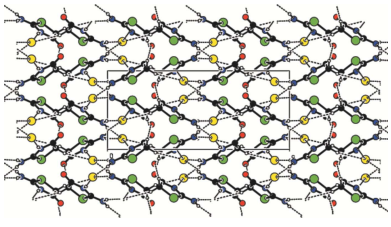
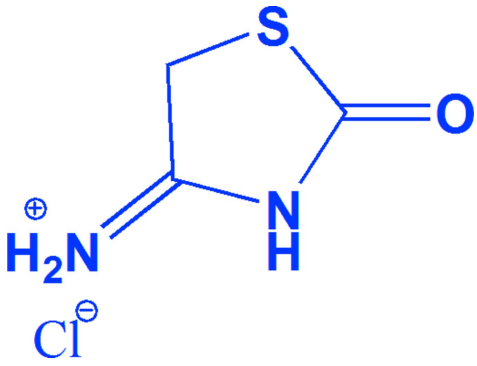
In the redetermination of the title compound, $C_3H_5N_2OS^+\cdot Cl^-$, the asymmetric unit consists of one independent 2-oxo-1,3-thiazolidin-4-iminium cation and one independent chloride anion. The cation interacts with a chloride anion *via* N—H···Cl hydrogen bonds forming a supramolecular chain along [010]. These supramolecular chains are further extended by weak C—H···Cl and C—H···O interactions, forming a two-dimensional network parallel to (001). The crystal structure is further stabilized by weak C—O···π interactions, supporting a three-dimensional architecture. The structure was previously determined by Ananthamurthy & Murthy [*Z. Kristallogr.* (1975). **8**, 356–367] but has been redetermined with higher precision to allow the hydrogen-bonding patterns and supramolecular interactions to be investigated.

1. Chemical context

Thiourea and its derivatives are an important group of organic compounds because of their diverse application in fields such as medicine, agriculture, coordination, and analytical chemistry (Saeed *et al.*, 2010, 2014). The complexes with thiourea derivatives expressing biological activity have been successfully screened for various biological actions such as antibacterial, antifungal, anticancer, antioxidant, anti-inflammatory, antimalarial, antiviral activity, as anti-HIV agents and also as catalysts (Saeed *et al.*, 2010). Thiazolidine derivatives show antitumor activity as well as a broad range of biological activities including antibactericidal, fungicidal, anti-angiogenesis, antidiabetic and antimicrobial (Singh *et al.*, 1981; Saeed & Florke, 2006; Rizos *et al.*, 2016). Thiourea derivatives are used as phase-change materials for thermal energy storage (Alkan *et al.*, 2011). In addition, metal complexes of thiourea derivatives are also studied for their relationship to NLO materials (Rajasekaran *et al.*, 2003; Ushasree *et al.*, 2000). Thiourea derivatives find applications related to their uses as synthons in supramolecular chemistry (Saeed & Florke, 2006). Organic and inorganic complexes of thiourea derivatives form well-defined non-covalent supramolecular architectures *via* multiple hydrogen bonds involving the N, S and O atoms. We report herein the molecular structure and supramolecular architecture of the title salt, $C_3H_5N_2SO^+Cl^-$, (I), formed from the reaction of thiourea with monochloro acetic acid. A determination of this crystal structure was performed by Ananthamurthy & Murthy (1975). However, while the authors could identify the space group as *Pbca* and determine the cell



parameters [a = 9.53 (1), b = 17.61 (5), c = 7.71 (1) Å], these were not accurate enough to examine the hydrogen-bonding patterns and supramolecular interactions that are described here.



2. Structural commentary

The asymmetric unit of the title compound (I) consists of one 2-imino-4-oxo-1,3-thiazolidine cation and one hydrochloride anion (Fig. 1). In the cation, the C3═N1 bond has double-bond character. The C3—N1 and C3—N2 bond distances indicate tautomerism between the amino N1 and imino N2 groups. The exocyclic bond [C3—N1 = 1.2930 (17) Å] is short and its length is comparable with that of the endocyclic C3—N2 bond [1.3432 (16) Å], confirming the C3═N1 double-bond assignment. The bond lengths and angles agree with those reported for similar structures (Ananthamurthy & Murthy, 1975; Xuan *et al.*, 2003; Vedavathi & Vijayan, 1981).

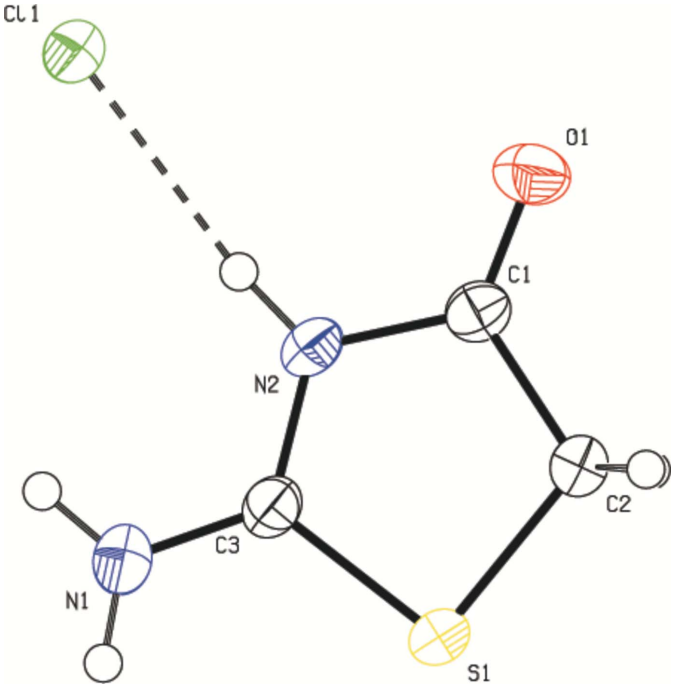


Figure 1
Asymmetric unit of the title compound, showing the atom-numbering scheme and 50% probability displacements ellipsoids. The dashed line represents the N2—H4···Cl1 hydrogen bond.

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

*Cg*1 is the centroid of the S1/N1/C1–C3 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl1^{i}	0.86	2.32	3.1484 (15)	162
N1—H3···Cl1^{ii}	0.86	2.34	3.1903 (15)	170
N2—H4···Cl1	0.86	2.26	3.1026 (12)	166
C2—H2···Cl1^{iii}	0.97	2.78	3.7137 (14)	163
C2—H5···O1^{iv}	0.97	2.57	3.5190 (18)	165
C1—O1···*Cg*1^{v}	1.20 (1)	3.13 (1)	3.9430 (15)	125 (1)

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

3. Supramolecular features

The 2-imino-4-oxo-1,3-thiazolidine cation interacts with the chlorine anion in the asymmetric unit *via* the N2—H4···Cl hydrogen bond (Table 1) and with symmetry-related Cl^-anions *via* N1—H1···Cl and N1—H3···Cl hydrogen bonds, forming supramolecular chains along [010] (Fig. 2). The chlorine anion interacts with the N2 atom and the exocyclic N1 atom of the thiazolidine moiety through the N2—H4···Cl

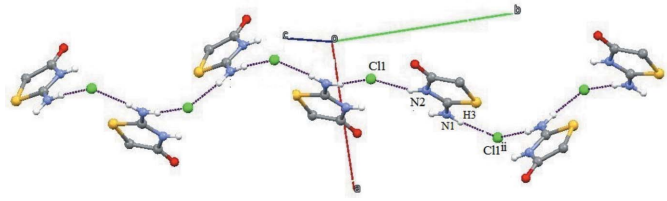


Figure 2
A view of a chain formed by N—H···Cl hydrogen bonds (dashed lines). Symmetry code as in Table 1.

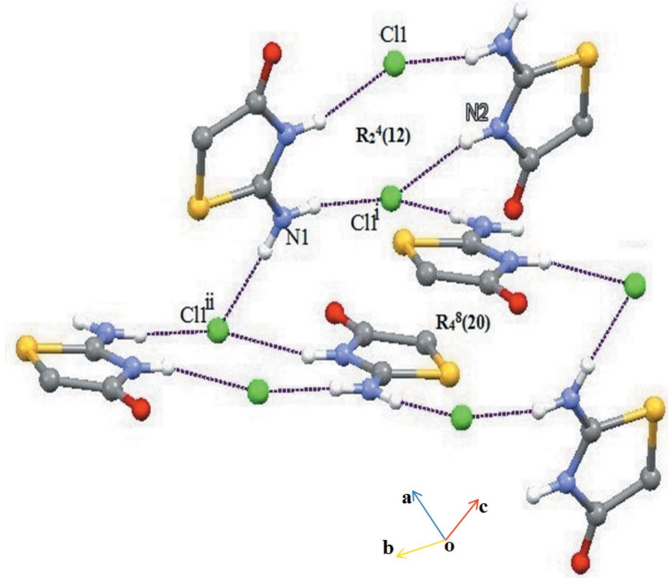


Figure 3
A view of the two supramolecular $R_2^4(12)$ and $R_4^8(20)$ ring motifs in the structure of (I), formed by N—H···Cl hydrogen bonds (dashed lines). Symmetry codes are given in Table 1.

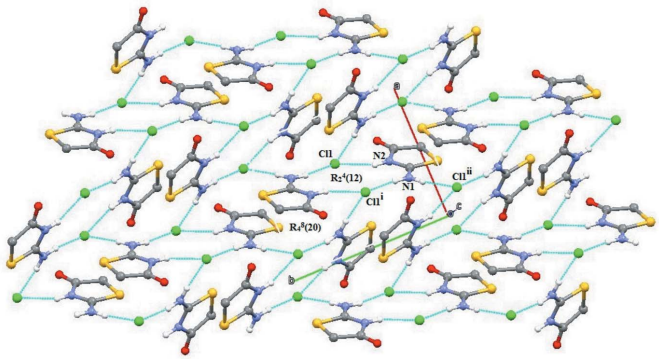


Figure 4
A view of the supramolecular sheet-like structures within the crystal packing of (I). Green dashed lines indicate N—H···Cl hydrogen bonds. Symmetry codes are given in Table 1.

hydrogen bond and the pair of N1—H1···Cl and N1—H3···Cl hydrogen bonds, forming $R_2^4(12)$ ring motifs in the [010] plane (Fig. 3). This motif is further connected on the other side by $R_4^8(20)$ ring motifs, generating a sheet-like structure parallel to (001) (Fig. 4). The supramolecular sheets and crystal packing are further stabilized by weak C—H···Cl, C—H···O and C=O···π interactions (Table 1, Fig. 5). All of these interactions combine to generate a three-dimensional supramolecular architecture (Fig. 6).

4. Database survey

The crystal structures of a number of related and substituted thiourea derivatives and thiazoline salts and their metal complexes have also been investigated in a variety of crystalline environments. These include DL-2-amino-2-thiazoline-4-carboxylic acid trihydrate (Xuan *et al.*, 2003), 2-amino-1,3-thiazoline hydrochloride (Vedavathi & Vijayan, 1981), *N*-(4-chlorobenzoyl)-*N*,*N*-diphenylthiourea (Arslan *et al.*, 2003*a*), 1-(4-chloro-benzoyl)-3-naphthalen-1-yl-thiourea (Arslan *et al.*, 2003*b*) and 1–(4–chlorophenyl)–3–(4–μethylbenzoyl)thiourea

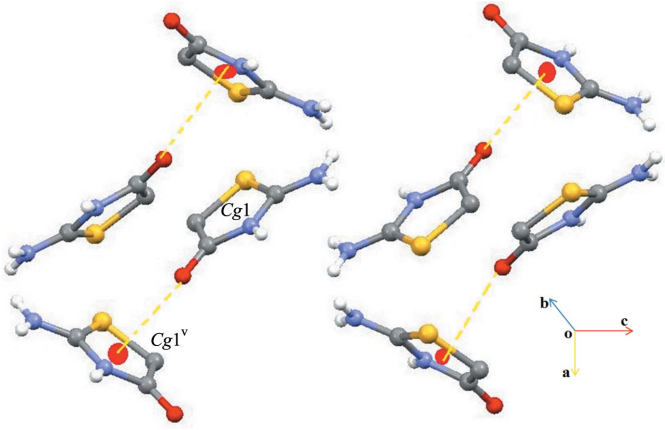


Figure 5
A view of the weak C—O···π interactions (dashed lines) in (I). *Cg*1 is the centroid of the thiazolidine ring. Symmetry codes are given in Table 1.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_3H_5N_2OS^+\cdot Cl^-$
M_r	152.60
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	296
a, *b*, *c* (Å)	7.5106 (11), 9.3140 (13), 17.343 (3)
V (Å^3)	1213.2 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.87
Crystal size (mm)	0.54 × 0.45 × 0.25
Data collection	
Diffractometer	Bruker SMART APEXII DUO CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.683, 0.832
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7517, 1798, 1554
R_{int}	0.020
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.708
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.077, 1.05
No. of reflections	1798
No. of parameters	73
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.33, −0.22

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXTL* (Sheldrick, 2008), *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

(Saeed & Floörke, 2006). N—H···Cl hydrogen bonds play a major role in building up the supramolecular architectures of many related crystal structures (for examples, see: Diallo *et al.*, 2014; Yamuna *et al.*, 2014; Plater & Harrison, 2016; Khongsuk *et al.*, 2015).

5. Synthesis and crystallization

Hot ethanol solutions of thiourea (32 mg) and chloro acetic acid (37 mg) were mixed in a 1:1 molar ratio. The resulting solution was warmed over a water bath for half an hour and then kept at room temperature for crystallization. After a week, light-yellow prismatic crystals suitable for single-crystal X-ray analysis were obtained.

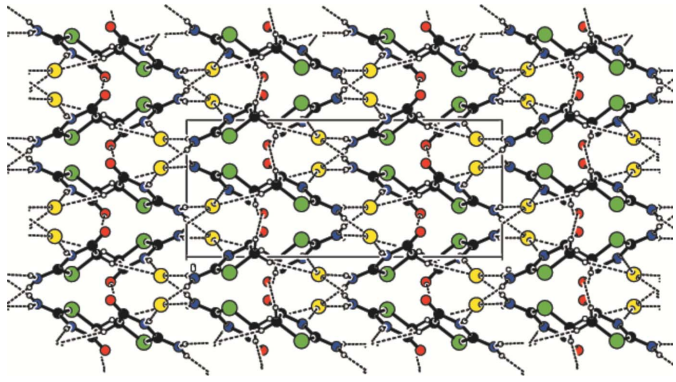


Figure 6
A view of the three-dimensional architecture of the title compound.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were initially located in difference-Fourier maps and were subsequently treated as riding atoms in geometrically idealized positions, with C—H = 0.93 and N—H = 0.86 and with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

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supporting information

Acta Cryst. (2019). E**75**, 443-446 [https://doi.org/10.1107/S2056989019003189]

Redetermination of the crystal structure of 2-oxo-1,3-thiazolidin-4-iminium chloride

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Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009).

2-Oxo-1,3-thiazolidin-4-iminium chloride

Crystal data

$C_3H_5N_2OS^+\cdot Cl^-$
M_r = 152.60
Orthorhombic, *Pbca*
a = 7.5106 (11) Å
b = 9.3140 (13) Å
c = 17.343 (3) Å
V = 1213.2 (3) Å^3
Z = 8
F(000) = 624
D_x = 1.671 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 1800 reflections
θ = 2.4–30.2°
μ = 0.87 mm^{-1}
T = 296 K
Prism, yellow
0.54 × 0.45 × 0.25 mm

Data collection

Bruker SMART APEXII DUO CCD area detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2009)
T_{min} = 0.683, T_{max} = 0.832
7517 measured reflections
1798 independent reflections
1554 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 30.2°, θ_{min} = 2.4°
h = −10→10
k = −10→13
l = −24→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.077
S = 1.05
1798 reflections
73 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-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0384P)^2 + 0.4007P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-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.

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.37439 (5)	−0.01239 (4)	0.86421 (2)	0.03155 (11)
O1	0.67766 (16)	0.25652 (11)	0.75866 (7)	0.0389 (2)
N1	0.3380 (2)	0.18329 (15)	0.97467 (7)	0.0409 (3)
H1	0.3567	0.2663	0.9949	0.049*
H3	0.2747	0.1209	0.9988	0.049*
C3	0.40497 (18)	0.15240 (14)	0.90803 (7)	0.0270 (3)
C2	0.51618 (18)	0.03829 (13)	0.78499 (7)	0.0272 (3)
H5	0.6172	−0.0263	0.7817	0.033*
H2	0.4507	0.0336	0.7368	0.033*
C1	0.57886 (18)	0.18932 (13)	0.79961 (7)	0.0264 (3)
N2	0.50511 (14)	0.24392 (11)	0.86677 (6)	0.0268 (2)
H4	0.5224	0.3312	0.8812	0.032*
Cl1	0.63837 (5)	0.54422 (4)	0.91839 (2)	0.03440 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0393 (2)	0.02303 (17)	0.03232 (19)	−0.00807 (13)	0.00667 (13)	−0.00457 (12)
O1	0.0438 (6)	0.0310 (5)	0.0418 (6)	−0.0042 (5)	0.0099 (5)	0.0066 (4)
N1	0.0593 (9)	0.0310 (6)	0.0325 (6)	−0.0057 (6)	0.0111 (6)	−0.0077 (5)
C3	0.0311 (6)	0.0224 (5)	0.0275 (6)	−0.0007 (5)	−0.0013 (5)	−0.0025 (4)
C2	0.0301 (6)	0.0255 (6)	0.0261 (6)	−0.0020 (5)	0.0015 (5)	−0.0030 (4)
C1	0.0281 (6)	0.0223 (5)	0.0289 (6)	0.0021 (5)	−0.0022 (5)	0.0028 (4)
N2	0.0312 (5)	0.0188 (5)	0.0304 (5)	−0.0014 (4)	−0.0018 (4)	−0.0022 (4)
Cl1	0.0453 (2)	0.02841 (18)	0.02950 (18)	−0.00821 (13)	0.00436 (13)	−0.00460 (12)

Geometric parameters (Å, º)

S1—C3	1.7280 (13)	C3—N2	1.3432 (16)
S1—C2	1.8013 (14)	C2—C1	1.5049 (18)
O1—C1	1.2027 (17)	C2—H5	0.9700
N1—C3	1.2930 (17)	C2—H2	0.9700

N1—H1	0.8600	C1—N2	1.3865 (17)
N1—H3	0.8600	N2—H4	0.8600
C3—S1—C2	91.38 (6)	C1—C2—H2	110.2
C3—N1—H1	120.0	S1—C2—H2	110.2
C3—N1—H3	120.0	H5—C2—H2	108.5
H1—N1—H3	120.0	O1—C1—N2	123.48 (12)
N1—C3—N2	123.56 (12)	O1—C1—C2	125.45 (12)
N1—C3—S1	122.62 (11)	N2—C1—C2	111.06 (11)
N2—C3—S1	113.82 (9)	C3—N2—C1	116.00 (11)
C1—C2—S1	107.55 (9)	C3—N2—H4	122.0
C1—C2—H5	110.2	C1—N2—H4	122.0
S1—C2—H5	110.2		
C2—S1—C3—N1	−176.63 (14)	N1—C3—N2—C1	174.68 (14)
C2—S1—C3—N2	2.92 (11)	S1—C3—N2—C1	−4.87 (15)
C3—S1—C2—C1	−0.44 (10)	O1—C1—N2—C3	−176.60 (14)
S1—C2—C1—O1	179.02 (12)	C2—C1—N2—C3	4.40 (16)
S1—C2—C1—N2	−2.00 (13)		

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the S1/N1/C1–C3 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1^{i}	0.86	2.32	3.1484 (15)	162
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C1—O1···*Cg*1^{v}	1.20 (1)	3.13 (1)	3.9430 (15)	125 (1)

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