

Supramolecular motifs in the first structures of organic carboxylate salts of 1-(diaminomethylene)thiourea (HATU)

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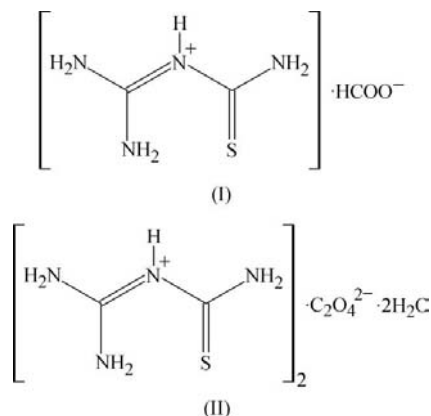
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The structures of the first two organic carboxylate salts of 1-(diaminomethylene)thiourea (HATU), namely 1-(diaminomethylene)thiuron-1-ium formate, $\text{C}_2\text{H}_7\text{N}_4\text{S}^+\cdot\text{HCOO}^-$, (I), and bis[1-(diaminomethylene)thiuron-1-ium] oxalate dihydrate, $2\text{C}_2\text{H}_7\text{N}_4\text{S}^+\cdot\text{C}_2\text{O}_4^{2-}\cdot 2\text{H}_2\text{O}$, (II), in which the oxalate lies on a symmetry centre, possess different extended hydrogen-bonding networks with different graph-set motifs. The $R_2^2(8)$ motif present in (I) does not appear in (II), but an $R_2^1(6)$ motif is present in both (I) and (II). Compound (I) has a three-dimensional hydrogen-bonding network, whereas (II) has a layered structure with layers joined by hydrogen-bonding motifs that form $R_4^2(8)$ patterns. This work extends the known supramolecular structural data for HATU to include these organic carboxylates in addition to the previously characterized salts with inorganic acids.

Comment

1-(Diaminomethylene)thiourea (HATU; Janczak & Perpétuo, 2008a; Hołyńska *et al.*, 2009) and its oxidation products (Hołyńska & Kubiak, 2008) are already considered to be useful building blocks in crystal engineering. To explore the possibility of HATU forming predictable hydrogen-bonding patterns, it would be useful to observe its behaviour towards other known building blocks. Carboxylates and carboxylic acids (Steiner, 2001) are widely used in this context. In particular, aggregation patterns have been studied for carboxylates of amino acids (*e.g.* Prasad & Vijayan, 1993). Other examples in this line of research include the structures of inclusion compounds based on thiourea and carboxylic acids (Li & Mak, 1997). Supramolecular motifs have been successfully utilized in tuning the nonlinear properties of a series of *N*-(2-aminoethyl)-4-nitroaniline adducts with carboxylic acids (Jaya Prakash & Radhakrishnan, 2006). Molecular recognition of carboxylates by guanidinium cations has also been investigated in biological systems (Best *et al.*,

2003). The crystal engineering of thioureas is still considered to be less developed than that of ureas (Custelcean, 2001).



The known crystal structures of 1-(diaminomethylene)thiuron-1-ium ($[\text{HATUH}]^+$) salts include hydrogen halides (Perpétuo & Janczak, 2008), perchlorate, hydrogen sulfate, dihydrogen phosphate and dihydrogen arsenate (Janczak & Perpétuo, 2008b), as well as hydrogen difluoride and hexafluoridosilicate (Hołyńska & Kubiak, 2009). None of these is a salt of an organic acid. In this paper, the crystal structures of two representative $[\text{HATUH}]^+$ carboxylates, *viz.* the formate, (I), and the oxalate dihydrate, (II), are described and

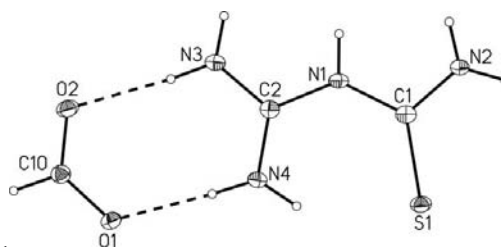


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.

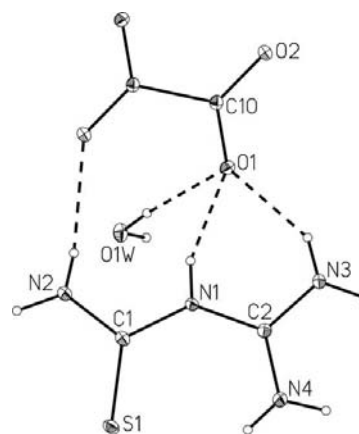
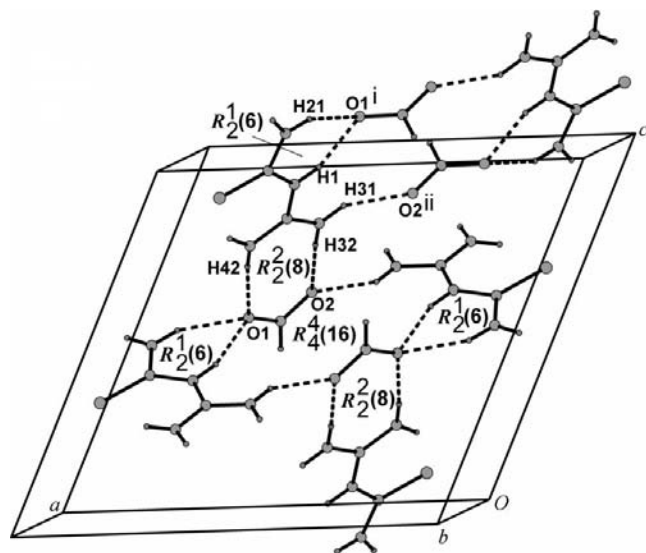


Figure 2
The structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. The unlabelled part of the oxalate is generated by the symmetry operation $(-x + 1, -y + 1, -z + 1)$.

**Figure 3**

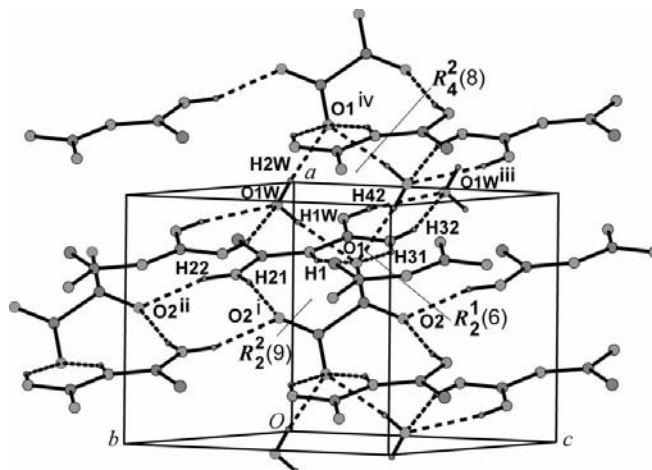
The three-dimensional hydrogen-bonding network in (I). Hydrogen bonds are shown as dashed lines and the graph-set motifs are marked. [Symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$.]

compared, with emphasis on the hydrogen-bonding motifs present.

Compounds (I) and (II) (Figs. 1 and 2) are the first structurally characterized organic [HATUH]⁺ carboxylates (Cambridge Structural Database; Version 5.30, with updates for February 2009; Allen, 2002). Compound (I) is the formate, whereas (II) is the oxalate, with the anion sitting astride a symmetry centre. These anions were chosen as being the simplest examples of mono- and dicarboxylate anions, and were expected to participate in different supramolecular motifs in the crystal structures. The results reported herein ratify these expectations. In contrast, however, the acetate salt, homologous with the formate salt, is also isomorphous with the latter (see *Experimental*), which underlines the role of the carboxylate group in motif formation in the crystal. Also, (II), in contrast with (I), incorporates water in the crystal structure, which further influences the hydrogen-bonding network.

The [HATUH]⁺ cation in both (I) and (II) is twisted, as previously observed for other salts of this cation (*e.g.* Janczak & Perpétuo, 2009*a*). The dihedral angle between the N1/C2/N3/N4 and N1/C1/N2/S1 planes is 5.5 (2)° for (I) and 4.5 (2)° for (II). These values are close to those calculated for the most stable conformation of [HATUH]⁺ by *ab initio* molecular orbital calculations (Table 1). The currently available data on [HATUH]⁺ salts show that the cation twisting may differ when different anions are used and is dependent on hydrogen bonding (Table 1). For the 1-(diaminomethylene)uron-1-ium cation in its hydrogen sulfate salt (Hołyńska & Kubiak, 2008) the analogous value is 1.8 (2)°.

The geometric parameters of the formate and oxalate anions in (I) and (II), respectively, do not deviate significantly from the reported values (*e.g.* melaminium formate; Perpétuo *et al.*, 2005). The oxalate anion, as in most of the available structures [*e.g.* bis(*N,N'*-diphenylguanidinium) oxalate; Paixão *et al.*, 1999], is flat and centrosymmetric. However,

**Figure 4**

The hydrogen-bonded layers and interlayer contacts in (II). Hydrogen bonds are shown as dashed lines. Cation H atoms not involved in hydrogen bonds have been omitted. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x, y, z - 1$; (iii) $x, y - 1, z$; (iv) $-x + 2, -y + 1, -z + 1$.]

there are also cases of twisted oxalate anions, *e.g.* in 4-ammonio-1-methylpiperazin-1-ium oxalate dihydrate (Guo, 2004) or in (*S,S*)-*N,N'*-bis(2-hydroxy-2-butyl)ethylenediammonium oxalate pentahydrate (Bai *et al.*, 2006).

The hydrogen-bonding patterns involving the carboxylate groups are different in (I) and (II). For (I), an $R_2^2(8)$ motif (Etter *et al.*, 1990) is formed by donation to the formate anion from the amino groups bonded to atom C2 (N3—H32...O2 and N4—H42...O1; Figs. 1 and 3 and Table 2). In (II), these amino groups do not participate in a similar motif; rather, they are donors in an $R_2^1(6)$ pattern [N3—H32...O1Wⁱⁱⁱ and N4—H42...O1Wⁱⁱⁱ, symmetry code (iii) as in Table 3]. However, a similar motif to $R_2^2(8)$ in (I) is the $R_2^2(9)$ motif in (II), created *via* participation of the central atom N1 and the N2 amino group of the cation as donors, and atoms O1 and O2ⁱ [symmetry code: (i) $1 - x, 1 - y, 1 - z$] from two different carboxyl groups of the centrosymmetric oxalate anion as acceptors (Figs. 2 and 4, and Table 3). It is interesting that the $R_2^1(6)$ motif present in (I) (Figs. 1 and 3), involving two hydrogen bonds with the central atom N1 and the N3 amino group of the cation as donors and a carboxylate O atom of the anion as acceptor, is robust enough to be retained in (II) (Fig. 4). This motif is also present in 1-(diaminomethylene)uron-1-ium hydrogen sulfate (Hołyńska & Kubiak, 2008).

A further structure-building principle is different in (I) and (II). Whereas in (I), subunits consisting of two formate anions and two [HATUH]⁺ cations, forming extended $R_4^4(16)$ motifs, can be distinguished (Fig. 3), in (II) a layered arrangement is present (Fig. 4). The hydrogen-bonded layers in (II) are connected *via* O—H...O hydrogen bonds (with a water molecule as donor and an oxalate anion as acceptor), which leads to the formation of $R_4^2(8)$ motifs consisting of two water molecules and two oxalate anions belonging to neighbouring layers. The presence of these specific contacts is possible since the plane of the oxalate anion interacting *via* the [HATUH]⁺ cation to form an $R_2^2(9)$ motif is inclined with respect to this cation [the dihedral angles to the two cation 'arms' are 40.8 (1)

and $42.6(1)^\circ$ for N1/C2/N3/N4 and N1/C1/N2/S1, respectively]. On the other hand, in (I) the formate anion plane is also somewhat inclined to the planes of the 'arms' of the interacting cation to form an $R_2^2(8)$ motif [the dihedral angles are $13.9(2)$ and $9.3(2)^\circ$ to N1/C2/N3/N4 and N1/C1/N2/S1, respectively].

Recently, Janczak & Perpétuo (2009) reported a new type of interaction in [HATUH]⁺ salts, claimed to be a π - π stacking of parallel [HATUH]⁺ cations separated by about 3.27 \AA . These interactions are said to stabilize the charge delocalization over the cation and significantly increase its planarity. In (II), the cations stack in an antiparallel fashion parallel to [100]. The N1/C1/N2/S1 arm of the molecule at $(2-x, -y, -z)$ eclipses the N1/C2/N3/N4 fragment of the molecule at (x, y, z) , with a dihedral angle of $4.5(2)^\circ$ and with the distances of the atoms of one fragment from the plane of the other lying within the range $3.18(1)$ – $3.39(1) \text{ \AA}$. The molecule at (x, y, z) also interacts with the molecule at $(1-x, -y, -z)$ [the relevant distances as defined above are in the range $3.08(1)$ – $3.35(1) \text{ \AA}$]. In (I), on the other hand, the cations are arranged in chains rather than stacks, extending along [010]. Although the extent of the postulated cation π - π interactions differs greatly between (I) and (II), the twisting of the cations in these structures is not much affected by this difference.

The presence of the S atom in the [HATUH]⁺ cation in (I) and (II) raises the question of whether there are hydrogen bonds with S as acceptor, although the importance of such interactions has been questioned (Allen *et al.*, 1997b). Nevertheless, there are authors motivated by the high S content in biological systems, who claim to utilize weak $D-H \cdots S$ (D = donor) interactions in crystal engineering. For example, Valdez-Martinez *et al.* (2004) claim to have successfully designed a strategy of constructing thiourea derivatives so as to avoid the formation of intramolecular hydrogen bonds. Such intramolecular N–H \cdots S hydrogen bonds seem to be present in the [HATUH]⁺ cation in (I) and (II) (Tables 2 and 3), as well as in other reported [HATUH]⁺ salts (*e.g.* Janczak & Perpétuo, 2009). Their formation is favoured based on considerations put forward by Etter *et al.* (1990) for six-membered hydrogen-bonded rings; the presence of the C=S bond makes it possible for some resonance-assisted stabilization to occur. Also, Allen *et al.* (1997a) discuss the possibility of resonance-induced hydrogen-bond formation with the S atom of a C=S group with N substituents. In (I) and (II), additional weak N–H \cdots S interactions seem to occur. However, in both cases the 'hydrogen bonds' involving S seem to be driven by the stronger hydrogen bonds present (Tables 2 and 3).

This study confirms the usefulness of HATU as a building block in crystal engineering and demonstrates its interaction with carboxylate, another common building block. Further insight into this field might be gained through examination of HATU-derivative carboxylate salts. We hope that the data for the simplest carboxylate and dicarboxylate [HATUH]⁺ salts will be useful in the design and description of new organic materials based on HATU ligand derivatives, which are worth investigating due to their potentially interesting properties

and structures. The results of this study imply that the $R_2^1(6)$ graph-set motif (Etter *et al.*, 1990) may be of importance in these investigations, but further conclusions await the analysis of different carboxylates.

Experimental

For the preparation of (I), HATU (0.05 g) was dissolved in an excess of 5% formic acid. On slow evaporation of the solution, crystals of (I) in the form of colourless plates were obtained. A similar procedure using acetic acid instead of formic acid yields crystals of the isomorphous acetate salt [$a = 11.978(4) \text{ \AA}$, $b = 6.208(3) \text{ \AA}$, $c = 11.753(4) \text{ \AA}$, $\beta = 116.57(3)^\circ$, $P2_1/c$, $V = 781.6(5) \text{ \AA}^3$]. For the preparation of (II), HATU (0.5 g) was dissolved in water (10 ml). A stoichiometric amount of oxalic acid dihydrate was dissolved in water (15 ml). The two solutions were combined to yield a white crystalline precipitate. The mixture obtained was allowed to stand for a week for slow recrystallization. A single crystal in the form of a colourless polyhedron was chosen from the precipitate.

Compound (I)

Crystal data

$C_2H_7N_4S^+ \cdot CHO_2^-$	$V = 728.8(5) \text{ \AA}^3$
$M_r = 164.19$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 12.693(4) \text{ \AA}$	$\mu = 0.39 \text{ mm}^{-1}$
$b = 5.509(3) \text{ \AA}$	$T = 100 \text{ K}$
$c = 11.576(4) \text{ \AA}$	$0.19 \times 0.14 \times 0.04 \text{ mm}$
$\beta = 115.80(3)^\circ$	

Data collection

Kuma KM-4-CCD area-detector diffractometer	6097 measured reflections
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2006)	1774 independent reflections
$T_{\min} = 0.955$, $T_{\max} = 0.981$	1336 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.044$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.108$	$\Delta\rho_{\max} = 0.28 \text{ e \AA}^{-3}$
$S = 1.00$	$\Delta\rho_{\min} = -0.20 \text{ e \AA}^{-3}$
1774 reflections	
99 parameters	

Compound (II)

Crystal data

$2C_2H_7N_4S^+ \cdot C_2O_4^{2-} \cdot 2H_2O$	$\gamma = 91.02(3)^\circ$
$M_r = 362.40$	$V = 367.7(3) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 7.006(3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 7.221(3) \text{ \AA}$	$\mu = 0.41 \text{ mm}^{-1}$
$c = 7.837(3) \text{ \AA}$	$T = 100 \text{ K}$
$\alpha = 111.89(3)^\circ$	$0.24 \times 0.21 \times 0.13 \text{ mm}$
$\beta = 90.82(3)^\circ$	

Data collection

Kuma KM-4-CCD area-detector diffractometer	4151 measured reflections
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2006)	2114 independent reflections
$T_{\min} = 0.909$, $T_{\max} = 0.952$	1827 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.010$

Table 1

Currently available data on HATU and its salts: dihedral angles ($^{\circ}$) between the N1/C2/N3/N4 and N1/C1/N2/S1 planes.

Compound	Angle	Reference
HATU at room temperature	22.2 (1)	(a)
HATU at 100 K	19.4 (2)	(b)
HATU, <i>ab initio</i> calculations	6.2	(c)
[HATUH] ⁺ nitrate	7.2 (1)	(d)
[HATUH] ⁺ phosphonate monohydrate	3.7 (1)	(d)
[HATUH] ⁺ chloride	22.9 (1)	(c)
[HATUH] ⁺ bromide	15.2 (1)	(c)
[HATUH] ⁺ iodide	4.2 (1)	(c)
[HATUH] ⁺ chlorate(VII)	1.4 (1)	(e)
[HATUH] ⁺ hydrogen sulfate	9.8 (1)	(e)
[HATUH] ⁺ dihydrogen phosphate	4.4 (1)	(e)
[HATUH] ⁺ dihydrogen arsenate	2.1 (1)	(e)

References: (a) Janczak & Perpétuo (2008a); (b) Holyńska *et al.* (2009); (c) Perpétuo & Janczak (2008); (d) Janczak & Perpétuo (2009); (e) Janczak & Perpétuo (2008b).

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	136 parameters
$wR(F^2) = 0.077$	All H-atom parameters refined
$S = 1.00$	$\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$
2114 reflections	$\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$

All H atoms were found in difference Fourier maps. For (I), the formate H atom was refined as riding on its parent C atom. The remaining H atoms bonded to N atoms were first refined with restraints (DFIX; Sheldrick, 2008), with N—H = 0.870 (2) Å, and their positional parameters were subsequently constrained (AFIX 3). The highest final difference Fourier peak of $0.28 \text{ e } \text{\AA}^{-3}$ is located 0.78 Å from atom C1 and 0.91 Å from atom S1. In the case of (II), H-atom parameters were refined freely. In the final difference Fourier map, the highest peak of $0.44 \text{ e } \text{\AA}^{-3}$ was located on the oxalate C—C bond (0.79 Å from atom C10).

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005) and *SHELXTL-NT* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3194). Services for accessing these data are described at the back of the journal.

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Table 2

Hydrogen-bond geometry (Å, $^{\circ}$) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O1 ⁱ	0.87	1.87	2.708 (2)	162
N3—H31 \cdots O2 ⁱⁱ	0.87	2.04	2.838 (2)	152
N3—H32 \cdots O2	0.87	1.98	2.844 (3)	176
N2—H21 \cdots O1 ⁱ	0.87	2.14	2.918 (2)	148
N4—H42 \cdots O1	0.87	1.94	2.808 (3)	172
N4—H41 \cdots S1	0.87	2.29	3.039 (2)	144
N2—H22 \cdots S1 ⁱⁱⁱ	0.87	2.55	3.409 (2)	168

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

Table 3

Hydrogen-bond geometry (Å, $^{\circ}$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O1	0.83 (2)	2.05 (2)	2.835 (2)	157 (2)
N2—H21 \cdots O2 ⁱ	0.77 (2)	2.13 (2)	2.888 (2)	169 (2)
N2—H22 \cdots O2 ⁱⁱ	0.91 (2)	2.05 (2)	2.897 (2)	155 (2)
N3—H31 \cdots O1	0.85 (2)	2.14 (2)	2.893 (2)	148 (2)
N3—H32 \cdots O1W ⁱⁱⁱ	0.86 (2)	2.11 (2)	2.904 (2)	152 (2)
N4—H42 \cdots O1W ⁱⁱⁱ	0.84 (2)	2.20 (2)	2.954 (2)	151 (2)
O1W—H1W \cdots O1	0.78 (2)	2.10 (2)	2.874 (2)	174 (2)
O1W—H2W \cdots O1 ^{iv}	0.83 (2)	2.00 (2)	2.821 (2)	175 (2)
N4—H41 \cdots S1	0.80 (2)	2.41 (2)	3.026 (2)	135 (2)
N3—H32 \cdots S1 ^v	0.86 (2)	2.86 (2)	3.285 (2)	112 (2)

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

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