organic compounds

Z and E isomers of butenedioic acid with 2-amino-1,3-thiazole: 2-amino-1,3-thiazolium hydrogen maleate and 2-amino-1,3-thiazolium hydrogen fumarate

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Maleic acid and fumaric acid, the Z and E isomers of butenedioic acid, form 1:1 adducts with 2-amino-1,3-thiazole, namely 2-amino-1,3-thiazolium hydrogen maleate (2ATHM), $C_3H_5N_2S^+ \cdot C_4H_3O_4^-$, and 2-amino-1,3-thiazolium hydrogen fumarate (2ATHF), $C_3H_5N_2S^+ \cdot C_4H_3O_4^-$, respectively. In both compounds, protonation of the ring N atom of the 2-amino-1,3-thiazole and deprotonation of one of the carboxyl groups are observed. The asymmetric unit of 2ATHF contains three independent ion pairs. The hydrogen maleate ion of 2ATHM shows a short intramolecular O—H···O hydrogen bond with an O···O distance of 2.4663 (19) Å. An extensive hydrogen-bonded network is observed in both compounds, involving N—H···O and O—H···O hydrogen bonds. 2ATHM forms two-dimensional sheets parallel to the *ab* plane, extending as independent parallel sheets along the *c* axis, whereas 2ATHF forms two-dimensional zigzag layers parallel to the *bc* plane, extending as independent parallel layers along the *a* axis.

Comment

Many naturally occurring and synthetic thiazole derivatives exhibit biological activities, such as antibiotic, anti-inflammatory, antibacterial and anthelmintic properties (Metzger, 1984; Crews *et al.*, 1988; Shinagawa *et al.*, 1997; Shivarama Holla *et al.*, 2003). Crystal structures and hydrogen-bonding patterns of derivatives of 2-amino-1,3-thiazole have already been reported (Lynch, 2002; Lynch & McClenaghan, 2004, 2005; Glidewell *et al.*, 2004). Maleic acid, the Z isomer of butenedioic acid, is a simple building block in two- and three-dimensional supramolecular architectures (Bowes *et al.*, 2003; Jin *et al.*, 2003), and many crystal structures of 1:1 organic salts of maleic acid with organoamines have been reported to explain their aggregation patterns and hydrogen-bonding interactions (Alagar *et al.*, 2001; Rajagopal *et al.*, 2001; Lah &

Leban, 2003). In all such structures, the maleic acid exists in either a monoionized state or its fully deprotonated form. Fumaric acid, the *E* isomer of butenedioic acid, is a key intermediate in the biosynthesis of organic acids (Natarajan *et al.*, 2009). An extensive network of hydrogen bonding has been observed in the majority of the crystal structures of salts of fumaric acid (Alagar *et al.*, 2003; Natarajan *et al.*, 2009; Büyükgüngör *et al.*, 2004).

The present study reports the structures of 2ATHM and 2ATHF, 1:1 organic salts of 2-amino-1,3-thiazole with the *Z* and *E* isomers of butenedioic acid, respectively. This work is a continuation of the study of the salts of the *Z* and *E* isomers of butenedioic acid with 8-hydroxyquinoline reported from our laboratory recently (Franklin & Balasubramanian, 2009). The crystal structure of the salt of 2-amino-1,3-thiazole with succinic acid has also been reported by us recently (Fun *et al.*, 2009). In the present study, the effect of the isomers on the conformational features and hydrogen-bonding networks in the 2-amino-1,3-thiazole adducts are analysed and compared with those of related structures.
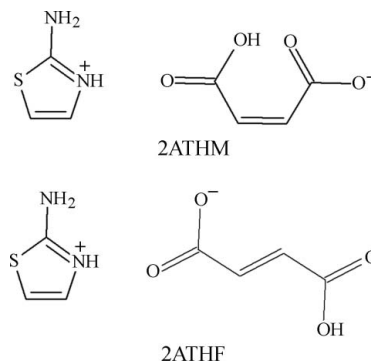
The molecular structures of 2ATHM and 2ATHF are shown in Figs. 1 and 2, respectively. The asymmetric unit of 2ATHM consists of a semimaleate anion and a 2-amino-1,3-thiazolium cation, while that of 2ATHF consists of three independent semifumarate anions and 2-amino-1,3-thiazolium cations. The 2-amino-1,3-thiazolium cations in both compounds are protonated at their ring N atoms, which is confirmed by the widening of the internal C—N—C angle from the value in neutral 2-amino-1,3-thiazole (Caranoni & Reboul, 1982) (Table 1). A similar geometry was observed in 2,2′-diamino-
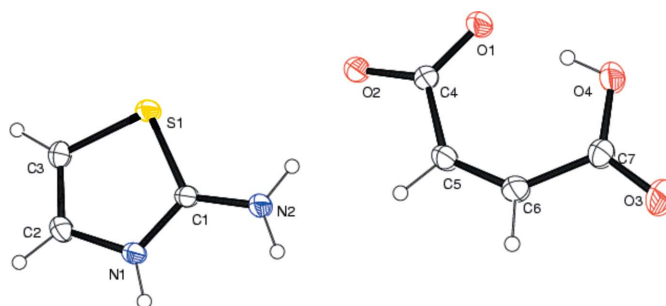

Figure 1
The molecular structure of 2ATHM, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.
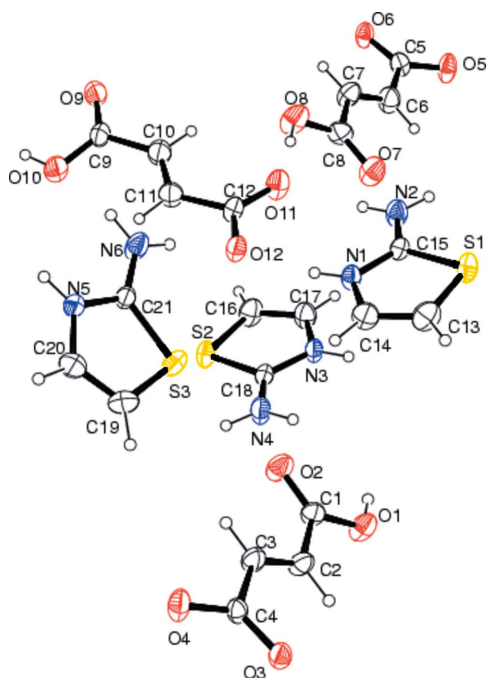
Figure 2
The molecular structure of 2ATHF, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

4,4′-bi-1,3-thiazolium fumarate (Liu *et al.*, 2003). There is an increase in the C—S—C bond angles and a decrease in the N—C—S bond angles of the cations of 2ATHM and 2ATHF from the value in neutral 2-amino-1,3-thiazole (Caranoni & Reboul, 1982) (Table 1). These observed values are comparable with those found in bis(2-amino-1,3-thiazolium) succinate succinic acid (Fun *et al.*, 2009).

The 2-amino-1,3-thiazolium ring of 2ATHM is essentially planar, with the maximum deviation from planarity being 0.007 (1) Å for atom C1. Similarly, the three 2-amino-1,3-

thiazolium rings of 2ATHF are essentially planar, with the maximum deviations from planarity being 0.004 (3) Å for atom C14, 0.006 (3) Å for atom C18 and 0.003 (3) Å for atom C21. The semimaleate and semifumarate anions are almost planar. The angle between the planes of the two halves of the semimaleate anion in 2ATHM (O1/O2/C4/C5 and O3/O4/C6/C7) is 5.81 (12)°, while the angles between the planes of two halves of the three semifumarate anions in 2ATHF are 11.76 (18)° for O1/O2/C1/C2 and O3/O4/C3/C4, 16.3 (2)° for O5/O6/C5/C6 and O7/O8/C7/C8, and 13.47 (19)° for O9/O10/C9/C10 and O11/O12/C11/C12.

Extensive networks of N—H···O and O—H···O hydrogen bonds (Tables 2 and 3) are observed to stabilize the crystal packing of both 2ATHM and 2ATHF. Parts of the crystal packing of the molecules, depicting the hydrogen-bonding interactions and various hydrogen-bonded motifs formed in 2ATHM and 2ATHF, are shown in Figs. 3 and 4, respectively. In 2ATHM, an intramolecular hydrogen bond between atoms O1 and O4 of the semimaleate anion is asymmetric and generates an $S(7)$ motif (Bernstein *et al.*, 1995), as observed in 8-hydroxyquinolinium hydrogen maleate (Franklin & Balasubramanian, 2009). This intramolecular hydrogen bond with an $S(7)$ motif is a common occurrence in several salts of maleate (Alagar *et al.*, 2001, 2002; Rajagopal *et al.*, 2001, 2002). The corresponding intramolecular hydrogen bond with an $S(5)$ motif is found in the semifumarate anion of 8-hydroxyquinolinium hydrogen fumarate (Franklin & Balasubramanian, 2009) but is not observed here in the semifumarate anions of 2ATHF. The two structures here differ, with intermolecular hydrogen-bonding interactions observed between the semifumarate anions in 2ATHF but not between the semimaleate anions in 2ATHM. In both 2ATHM and 2ATHF, the N_{amine} and N_{ring} atoms of the 2-amino-1,3-thiazolium cations are linked to the deprotonated carboxylate groups of the anions through strong N—H···O hydrogen bonds, to form a common cyclic ring motif denoted by $R_2^2(8)$. Similar $R_2^2(8)$ motifs have
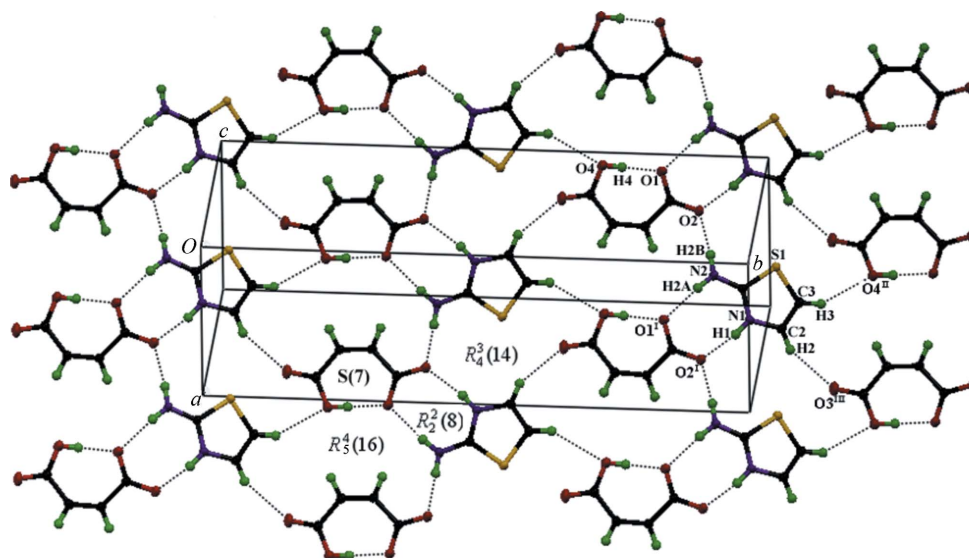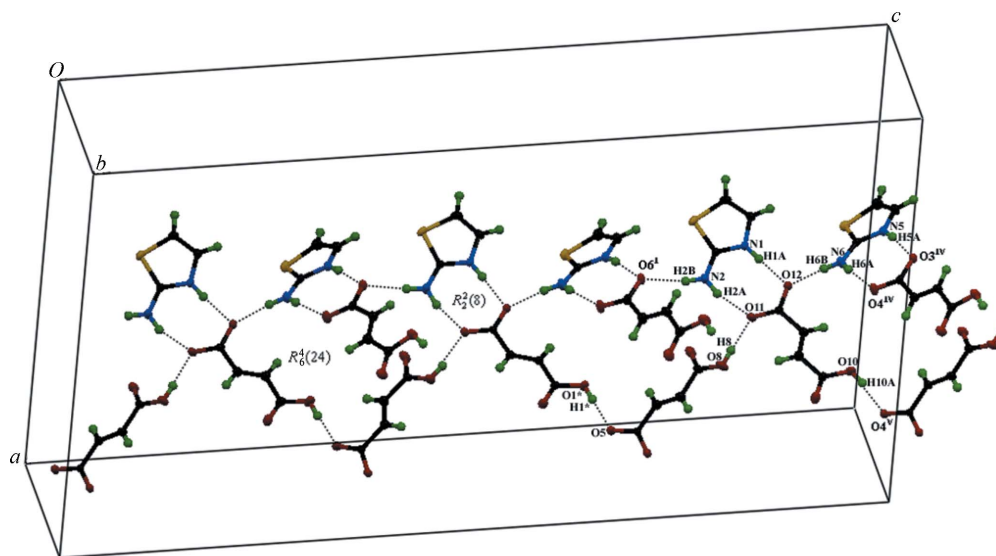

Figure 3
Part of the crystal structure of 2ATHM, showing the formation of the hydrogen-bonded sheet parallel to the *ab* plane built from $R_2^2(8)$, $R_5^4(16)$ and $R_4^3(14)$ motifs. Dotted lines indicate hydrogen bonds. [Symmetry codes: (I) $x + 1, y, z$; (II) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (III) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.]
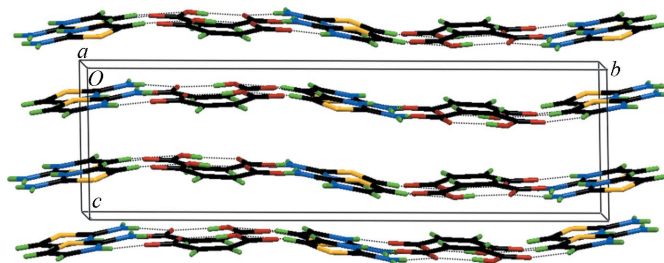
Figure 4
Part of the crystal structure of 2ATHF, showing the formation of the anionic chain along the [001] direction and the formation of $R_2^2(8)$, $R_6^4(24)$ and $D_2^2(9)$ motifs. Dotted lines indicate hydrogen bonds. [Symmetry codes: (I) $-x + \frac{3}{2}, y - \frac{1}{2}, z$; (IV) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$; (V) $-x + 1, -y + 1, -z + 2$; (*) $x + \frac{1}{2}, y, -z + \frac{3}{2}$.]

been observed in the vast majority of adducts/organic salts comprising a 2-amino heterocycle and a carboxylic acid molecule (Lynch, 2004; Büyükgüngör *et al.*, 2004; Fun *et al.*, 2009).

In 2ATHM, a pair of 2-amino-1,3-thiazolium cations is linked to a pair of maleate anions through N_{amine}—H···O and N_{ring}—H···O hydrogen bonds, in which the acceptor O atom forms a bifurcated interaction (entries 3 and 4 in Table 2), along with two C—H···O interactions (entries 5 and 6 in Table 2), resulting in a supramolecular ring motif of type $R_4^3(14)$. Two N_{amine}—H···O hydrogen bonds (entries 2 and 3 in Table 2) and two C—H···O interactions (entries 5 and 6 in Table 2), along with an intramolecular O—H···O hydrogen bond, form a ring motif of type $R_5^4(16)$. The combination of these interactions with two other supramolecular $R_2^2(8)$ and $R_4^3(14)$ motifs forms two-dimensional sheets extending parallel to the *ab* plane (Fig. 5). The overall packing of the structure consists of supramolecular sheets built from anions and cations stacked discretely one above the other along the [001] direction.

In 2ATHF, a very simple one-dimensional substructure is generated by an intermolecular interaction between the anions alone. A second-level graph-set motif of $D_2^2(9)$ (Sudbeck *et al.*, 1995) is formed by three independent fumarate anions linked through O—H···O hydrogen bonds (entries 8 and 12 in Table 3). These $D_2^2(9)$ motifs are linked through an O—H···O hydrogen bond (entry 7 in Table 3), forming a one-dimensional anionic chain extending along the [001] direction. A similar one-dimensional anionic chain is observed in most of the fumarate salts (Franklin & Balasubramanian, 2009; Bowes *et al.*, 2003; Büyükgüngör *et al.*, 2004). The cations are linked to these anionic chains through N—H···O hydrogen bonds to form a ring motif of type $R_6^4(24)$. These alternately fused $R_2^2(8)$ (mentioned earlier) and $R_6^4(24)$ supramolecular motifs combine with the $D_2^2(9)$ motif to generate a two-dimensional hydrogen-bonded zigzag layer

Figure 5
The two-dimensional hydrogen-bonded sheets of 2ATHM, perpendicular to the *c* axis. Dotted lines indicate hydrogen bonds.
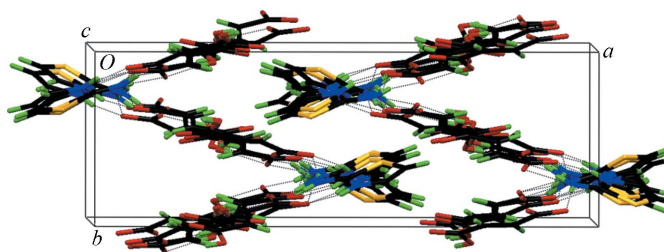
Figure 6
The two dimensional hydrogen-bonded zigzag layers of 2ATHF, perpendicular to the *a* axis. Dotted lines indicate hydrogen bonds.

extending parallel to the *bc* plane (Fig. 6). This matrix extends along the [100] direction as parallel independent layers, with no classical hydrogen bonds observed to bind the layers.

Experimental

Equimolar quantities of 2-amino-1,3-thiazole (0.3 g, 3 mmol) and maleic acid (0.35 g, 3 mmol) were dissolved in water and stirred. Concentrated hydrochloric acid (2 ml) was added and the mixture was refluxed at 333 K for 6 h. Brown crystals of 2ATHM (m.p. 429 K)

were harvested after a month from the slow evaporation of the solvent. Similarly, equimolar quantities of 2-amino-1,3-thiazole (0.3 g, 3 mmol) and fumaric acid (0.35 g, 3 mmol) were dissolved in acetonitrile and stirred. Dilute hydrochloric acid (0.5 M, 2 ml) was added and the stirred solution was refluxed at 333 K for 6 h. Brown crystals of 2ATHF (m.p. 457 K) were harvested from the resulting solution after two weeks of solvent evaporation.

2ATHM

Crystal data

$C_3H_5N_2S^+ \cdot C_4H_3O_4^-$
$M_r = 216.21$
Monoclinic, $P2_1/n$
$a = 6.3372 (4)$ Å
$b = 22.4153 (14)$ Å
$c = 6.8618 (4)$ Å
$\beta = 111.112 (2)°$

$V = 909.29 (10)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.35$ mm^{-1}
$T = 292$ K
$0.28 \times 0.16 \times 0.08$ mm

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker 2004)
$T_{min} = 0.909$, $T_{max} = 0.973$

11445 measured reflections
2529 independent reflections
2056 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.117$
$S = 1.06$
2529 reflections

128 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

2ATHF

Crystal data

$C_3H_5N_2S^+ \cdot C_4H_3O_4^-$
$M_r = 216.21$
Orthorhombic, $Pbca$
$a = 20.7129 (5)$ Å
$b = 7.1803 (2)$ Å
$c = 37.4469 (9)$ Å

$V = 5569.3 (2)$ Å^3
$Z = 24$
Mo $K\alpha$ radiation
$\mu = 0.34$ mm^{-1}
$T = 292$ K
$0.3 \times 0.2 \times 0.2$ mm

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker 2004)
$T_{min} = 0.905$, $T_{max} = 0.935$

44583 measured reflections
5302 independent reflections
4161 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.149$
$S = 1.04$
5302 reflections

382 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

The positions of H atoms bound to N and O atoms were identified from difference electron-density maps and then constrained in idealized positions. For 2ATHM, these H atoms were allowed to ride on the parent atom, with N—H = 0.86 Å and O—H = 0.82 Å, and with $U_{iso}(H) = 1.2U_{eq}(N,O)$. For 2ATHF, the O—H positions were allowed to rotate around the C—O bond, with O—H = 0.82 Å and $U_{iso}(H) = 1.5U_{eq}(O)$, and the H atoms on N atoms were allowed to ride, with N—H = 0.86 Å and $U_{iso}(H) = 1.2U_{eq}(N)$. H atoms bound to C atoms were treated as riding, with C—H = 0.93 Å and $U_{iso}(H) =$

Table 1
Comparison of selected geometric parameters of 2ATHM and 2ATHF with neutral 2-amino-1,3-thiazole (Å, °).

In all cases, the N atom is that in the thiazole ring.

	Neutral 2-amino-1,3-thiazole	2ATHM	2ATHF (molecule A)	2ATHF (molecule B)	2ATHF (molecule C)
C—N—C	109.40 (5)	113.79 (13)	114.0 (2)	113.4 (2)	113.5 (2)
C—S—C	88.60 (3)	90.39 (8)	90.31 (14)	90.47 (14)	90.16 (14)
N—C—S	114.9 (5)	111.41 (12)	110.93 (18)	111.15 (18)	111.23 (19)
N—C	1.298 (6)	1.324 (19)	1.326 (3)	1.331 (3)	1.329 (3)
			(N1—C1)	(N1—C15)	(N3—C18)	(N5—C21)

Table 2
Hydrogen-bond geometry (Å, °) for 2ATHM.

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O1	0.82	1.65	2.4663 (19)	175
N2—H2A···O1^i	0.86	2.01	2.8618 (19)	174
N2—H2B···O2	0.86	2.01	2.8453 (19)	164
N1—H1···O2^i	0.86	1.91	2.7607 (18)	171
C3—H3···O4^{ii}	0.93	2.57	3.410 (2)	150
C2—H2···O3^{iii}	0.93	2.39	3.249 (2)	153

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

Table 3
Hydrogen-bond geometry (Å, °) for 2ATHF.

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2B···O6^i	0.86	2.02	2.860 (3)	167
N3—H3A···O6^{ii}	0.86	1.93	2.773 (3)	167
N4—H4A···O5^{ii}	0.86	1.95	2.748 (3)	155
N4—H4B···O3^{iii}	0.86	2.01	2.858 (3)	169
N5—H5A···O3^{iv}	0.86	1.93	2.775 (3)	168
N6—H6A···O4^{iv}	0.86	1.93	2.762 (3)	162
O1—H1···O5^{ii}	0.82	1.75	2.566 (3)	175
O10—H10A···O4^v	0.82	1.8	2.607 (3)	170
N1—H1A···O12	0.86	1.87	2.715 (3)	169
N2—H2A···O11	0.86	1.99	2.815 (3)	161
N6—H6B···O12	0.86	1.97	2.824 (3)	172
O8—H8···O11	0.82	1.75	2.572 (3)	175

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

$1.2U_{eq}(C)$. Three (for 2ATHM) and seven (for 2ATHF) outlier reflections were excluded from the intensity data.

For both compounds, data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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