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[(Dimethylamino)methyl]dimethylazanium bis(trifluoromethanesulfonyl)amide

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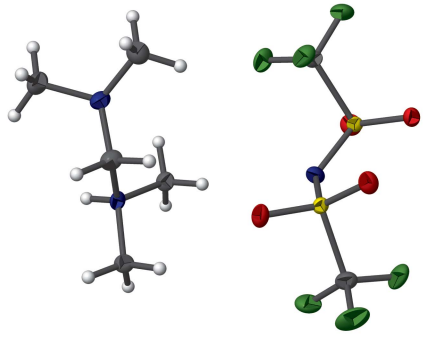
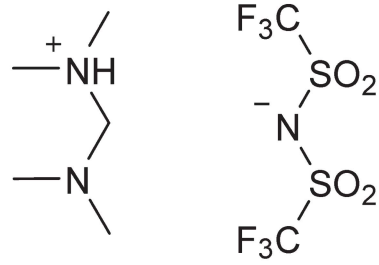
Structural data: full structural data are available from iucrdata.iucr.org

The title molecular salt, $C_5H_{15}N_2^+\cdot C_2F_6NO_4S_2^-$, was obtained by a proton transfer reaction between bis(trifluoromethanesulfonyl)amine and bis(dimethylamino)methane. In the crystal, the ions are linked by N—H···O═S hydrogen bonds, and these units are linked by C—H···O hydrogen bonds, forming sheets parallel to the *bc* plane. The crystal was refined as a non-merohedral twin with a BASF factor of 0.316 (1).

3D view



Chemical scheme



Structure description

The molecular structure of the title compound is shown in Fig. 1. The bis(dimethylamino)methane molecule is protonated resulting in a mono-cation. Bis(trifluoromethanesulfonyl)amides [also called 'bis(triflimides)'] are known to exist as either *syn* or *anti* conformers in the solid state (Bentivoglio *et al.*, 2009; Laus *et al.*, 2011). Here, the anion adopts an *anti* conformation with a C6—S1···S2—C7 torsion angle of 169.4 (1)°. The negative charge of the anion is effectively delocalized, thus bestowing only weak coordinating properties.

In the crystal, N—H···O═S hydrogen bonds link the ions and one strong and two weaker C—H···O═S hydrogen bonds link these units, forming sheets parallel to the *bc* plane (Figs. 2 and 3, Table 1). No direct contacts to the triflimide nitrogen N3 atom were detected.

This compound is another example of a low-melting, protic organic bis(triflimide) salt. Properties and applications of these protic Ionic Liquids (PILs) have been reviewed (Greaves & Drummond, 2008). The related structure of an organic liquid salt formed by a

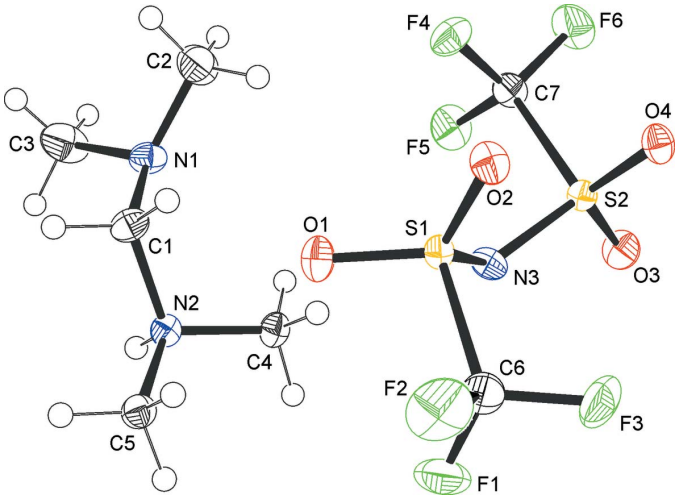


Figure 1
The molecular structure of the ion pair of the title molecular salt, with atom labelling and 50% probability displacement ellipsoids.

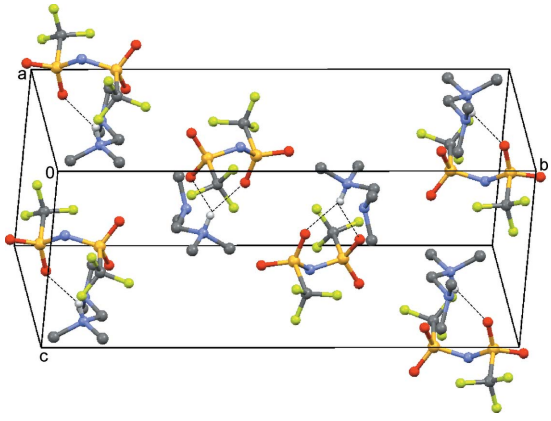


Figure 2
Crystal packing of the title molecular salt. Hydrogen atoms have been omitted for clarity, except those engaged in N—H···O hydrogen bonding (see Table 1).

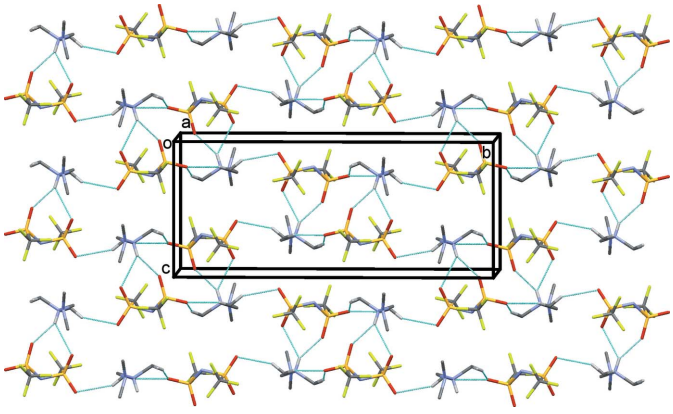


Figure 3
A view along the *a* axis of the crystal packing of the title molecular salt. The hydrogen bonds are shown as dashed lines (see Table 1), and, for clarity, only the H atoms involved in these interactions have been included.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O4^{i}	0.87 (2)	2.08 (2)	2.868 (3)	150 (2)
N2—H2···O2^{i}	0.87 (2)	2.46 (2)	3.115 (2)	133 (2)
C5—H5*A*···O3^{ii}	0.98	2.38	3.299 (3)	156
C4—H4*C*···O3^{ii}	0.98	2.59	3.444 (3)	145
C5—H5*B*···O1^{iii}	0.98	2.57	3.423 (3)	145

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_5H_{15}N_2^+\cdot C_2F_6NO_4S_2^-$
M_r	383.36
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	8.5071 (3), 20.9755 (8), 8.9099 (4)
β (°)	90.173 (3)
V (Å^3)	1589.88 (11)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.42
Crystal size (mm)	0.24 × 0.20 × 0.20
Data collection	
Diffractometer	Oxford Diffraction Gemini-R Ultra
Absorption correction	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)
T_{min}, T_{max}	0.907, 0.922
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9624, 2874, 2739
R_{int}	0.028
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.600
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.068, 1.06
No. of reflections	2874
No. of parameters	207
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.33, −0.29

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2008), *SIR2002* (Burla *et al.*, 2003), *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008).

proton-transfer reaction between bis(trifluoromethanesulfonyl)amine and dimethylformamide has been reported (Cardenas & O'Hagan, 2016).

Synthesis and crystallization

Bis(dimethylamino)methane (1.20 g, 11.7 mmol) was added dropwise to bis((trifluoromethane)sulfonyl)amine (3.30 g, 11.7 mmol). The mixture was stirred at room temperature to yield a viscous, colourless liquid. Suitable crystals were obtained by slow cooling (m.p. 280–283 K). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.45 (*s*, 12H), 3.63 (*s*, 2H), 6.9 (*br*, 1H) p.p.m. ^{13}C NMR (75 MHz, DMSO-d_6): δ 41.7, 80.7 (4 C), 119.5 (*q*, J = 322 Hz, 2C) p.p.m. IR (neat): ν 3172 (*w*), 2807 (*w*),

1345 (*m*), 1325 (*m*), 1179 (*s*), 1130 (*s*), 1052 (*s*), 790 (*w*), 741 (*w*), 612 (*m*), 570 (*m*), 510 (*m*) cm^{-1}.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The crystal was refined as a non-merohedral twin [180° rotation about *a**] with a BASF factor of 0.316 (1).

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full crystallographic data

IUCrData (2016). **1**, x161658 [https://doi.org/10.1107/S2414314616016588]

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Crystal data

$C_5H_{15}N_2^+·C_2F_6NO_4S_2^-$
M_r = 383.36
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 8.5071 (3) Å
b = 20.9755 (8) Å
c = 8.9099 (4) Å
β = 90.173 (3)°
V = 1589.88 (11) Å^3
Z = 4
$F(000)$ = 784
D_x = 1.602 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6860 reflections
θ = 3.0–28.3°
μ = 0.42 mm^{-1}
T = 100 K
Block, colourless
0.24 × 0.20 × 0.20 mm

Data collection

Oxford Diffraction Gemini-R Ultra diffractometer
Graphite monochromator
Detector resolution: 10.3822 pixels mm^{-1}
ω (1° width) scans
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2008)
T_{min} = 0.907, T_{max} = 0.922
9624 measured reflections
2874 independent reflections
2739 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 25.3°, θ_{min} = 3°
h = −10→8
k = −25→23
l = −9→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.068
S = 1.06
2874 reflections
207 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 0.4067P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 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	0.57434 (6)	0.14606 (2)	0.75790 (7)	0.01443 (13)
S2	0.72783 (7)	0.03241 (2)	0.83172 (7)	0.01478 (13)
F4	0.95493 (16)	0.11210 (6)	0.77018 (17)	0.0269 (3)
F5	0.94238 (18)	0.03106 (7)	0.62282 (16)	0.0310 (4)
F3	0.33176 (17)	0.09974 (8)	0.89895 (19)	0.0346 (4)
F6	1.03258 (17)	0.01977 (8)	0.84722 (18)	0.0357 (4)
F1	0.29633 (17)	0.11073 (8)	0.66095 (18)	0.0385 (4)
F2	0.29664 (19)	0.19311 (8)	0.8058 (2)	0.0440 (5)
O4	0.73015 (19)	0.05025 (7)	0.98655 (18)	0.0195 (4)
O3	0.7037 (2)	−0.03286 (7)	0.79420 (19)	0.0248 (4)
O1	0.5888 (2)	0.18332 (7)	0.62404 (18)	0.0221 (4)
O2	0.6286 (2)	0.17340 (7)	0.89653 (19)	0.0209 (4)
N3	0.6242 (2)	0.07529 (9)	0.7246 (2)	0.0174 (4)
C7	0.9264 (3)	0.04976 (11)	0.7639 (3)	0.0202 (5)
C6	0.3619 (3)	0.13647 (12)	0.7819 (3)	0.0243 (6)
N2	0.6602 (2)	0.13384 (9)	0.2322 (2)	0.0166 (4)
H2	0.673 (3)	0.1214 (12)	0.140 (2)	0.02*
N1	0.9399 (2)	0.15256 (9)	0.2565 (2)	0.0219 (4)
C2	1.0467 (3)	0.15839 (14)	0.3829 (3)	0.0329 (7)
H2A	1.0838	0.2025	0.3903	0.049*
H2B	1.1366	0.1299	0.3683	0.049*
H2C	0.9918	0.1467	0.4754	0.049*
C4	0.6675 (3)	0.07490 (11)	0.3251 (3)	0.0206 (5)
H4A	0.6492	0.0858	0.4306	0.031*
H4B	0.7715	0.0553	0.3149	0.031*
H4C	0.5867	0.0449	0.2911	0.031*
C3	1.0159 (3)	0.16873 (17)	0.1164 (3)	0.0367 (7)
H3A	0.9404	0.1645	0.0337	0.055*
H3B	1.1047	0.1399	0.0996	0.055*
H3C	1.054	0.2128	0.121	0.055*
C5	0.5036 (3)	0.16500 (11)	0.2400 (3)	0.0208 (5)
H5A	0.4219	0.1341	0.2128	0.031*
H5B	0.5003	0.2011	0.1701	0.031*
H5C	0.4854	0.1804	0.3424	0.031*
C1	0.7886 (3)	0.18053 (11)	0.2756 (3)	0.0218 (5)
H1A	0.7802	0.2192	0.2124	0.026*
H1B	0.7751	0.1934	0.3816	0.026*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0148 (3)	0.0143 (3)	0.0142 (3)	0.0019 (2)	0.0018 (3)	0.0008 (2)
S2	0.0148 (3)	0.0135 (3)	0.0160 (3)	0.0019 (2)	0.0006 (2)	0.0001 (2)
F4	0.0225 (7)	0.0283 (8)	0.0300 (8)	−0.0057 (6)	0.0071 (6)	−0.0016 (7)
F5	0.0340 (8)	0.0377 (9)	0.0214 (8)	0.0056 (7)	0.0094 (6)	−0.0062 (6)
F3	0.0291 (8)	0.0415 (10)	0.0334 (9)	−0.0058 (7)	0.0131 (7)	0.0096 (8)
F6	0.0195 (7)	0.0522 (10)	0.0354 (9)	0.0134 (7)	0.0000 (7)	0.0087 (8)
F1	0.0197 (8)	0.0589 (11)	0.0371 (9)	−0.0018 (7)	−0.0073 (7)	−0.0010 (9)
F2	0.0282 (9)	0.0378 (9)	0.0661 (13)	0.0166 (7)	0.0141 (8)	−0.0004 (8)
O4	0.0220 (9)	0.0202 (9)	0.0164 (8)	0.0048 (7)	0.0021 (7)	0.0015 (7)
O3	0.0300 (9)	0.0152 (8)	0.0293 (10)	0.0008 (7)	−0.0009 (8)	−0.0003 (7)
O1	0.0281 (10)	0.0203 (9)	0.0180 (9)	0.0019 (7)	0.0051 (7)	0.0026 (7)
O2	0.0270 (9)	0.0178 (9)	0.0180 (9)	0.0019 (7)	−0.0004 (7)	−0.0028 (7)
N3	0.0182 (9)	0.0174 (10)	0.0166 (10)	0.0030 (8)	−0.0027 (8)	−0.0041 (8)
C7	0.0160 (11)	0.0263 (13)	0.0183 (13)	0.0043 (10)	0.0025 (11)	−0.0012 (11)
C6	0.0187 (12)	0.0254 (14)	0.0288 (16)	0.0052 (10)	0.0018 (11)	0.0024 (11)
N2	0.0193 (10)	0.0178 (10)	0.0128 (11)	0.0000 (7)	0.0025 (9)	−0.0026 (8)
N1	0.0168 (10)	0.0270 (11)	0.0218 (10)	−0.0001 (8)	0.0021 (10)	−0.0036 (10)
C2	0.0278 (15)	0.0428 (17)	0.0281 (15)	0.0009 (13)	−0.0014 (12)	0.0035 (13)
C4	0.0227 (13)	0.0173 (12)	0.0220 (13)	−0.0001 (9)	0.0021 (11)	0.0022 (11)
C3	0.0265 (15)	0.063 (2)	0.0212 (15)	0.0016 (14)	0.0039 (12)	−0.0037 (14)
C5	0.0192 (12)	0.0198 (12)	0.0232 (13)	−0.0001 (9)	0.0002 (11)	0.0009 (12)
C1	0.0212 (12)	0.0188 (12)	0.0255 (14)	−0.0020 (10)	0.0019 (11)	−0.0047 (10)

Geometric parameters (Å, º)

S1—O1	1.4315 (17)	N1—C1	1.425 (3)
S1—O2	1.4368 (18)	N1—C3	1.448 (3)
S1—N3	1.5722 (19)	N1—C2	1.450 (3)
S1—C6	1.832 (3)	C2—H2A	0.98
S2—O3	1.4240 (16)	C2—H2B	0.98
S2—O4	1.4294 (17)	C2—H2C	0.98
S2—N3	1.578 (2)	C4—H4A	0.98
S2—C7	1.832 (2)	C4—H4B	0.98
F4—C7	1.331 (3)	C4—H4C	0.98
F5—C7	1.324 (3)	C3—H3A	0.98
F3—C6	1.322 (3)	C3—H3B	0.98
F6—C7	1.326 (3)	C3—H3C	0.98
F1—C6	1.327 (3)	C5—H5A	0.98
F2—C6	1.329 (3)	C5—H5B	0.98
N2—C5	1.486 (3)	C5—H5C	0.98
N2—C4	1.489 (3)	C1—H1A	0.99
N2—C1	1.516 (3)	C1—H1B	0.99
N2—H2	0.869 (17)		
O1—S1—O2	118.04 (10)	C1—N1—C2	115.9 (2)

O1—S1—N3	109.54 (10)	C3—N1—C2	111.67 (19)
O2—S1—N3	116.91 (10)	N1—C2—H2A	109.5
O1—S1—C6	104.14 (11)	N1—C2—H2B	109.5
O2—S1—C6	104.96 (11)	H2A—C2—H2B	109.5
N3—S1—C6	100.69 (11)	N1—C2—H2C	109.5
O3—S2—O4	118.68 (10)	H2A—C2—H2C	109.5
O3—S2—N3	109.04 (10)	H2B—C2—H2C	109.5
O4—S2—N3	116.12 (10)	N2—C4—H4A	109.5
O3—S2—C7	104.23 (11)	N2—C4—H4B	109.5
O4—S2—C7	104.85 (11)	H4A—C4—H4B	109.5
N3—S2—C7	101.60 (11)	N2—C4—H4C	109.5
S1—N3—S2	125.08 (13)	H4A—C4—H4C	109.5
F5—C7—F6	108.61 (19)	H4B—C4—H4C	109.5
F5—C7—F4	108.18 (19)	N1—C3—H3A	109.5
F6—C7—F4	108.59 (19)	N1—C3—H3B	109.5
F5—C7—S2	110.58 (16)	H3A—C3—H3B	109.5
F6—C7—S2	110.36 (16)	N1—C3—H3C	109.5
F4—C7—S2	110.45 (15)	H3A—C3—H3C	109.5
F3—C6—F1	108.8 (2)	H3B—C3—H3C	109.5
F3—C6—F2	108.2 (2)	N2—C5—H5A	109.5
F1—C6—F2	108.6 (2)	N2—C5—H5B	109.5
F3—C6—S1	110.45 (17)	H5A—C5—H5B	109.5
F1—C6—S1	111.24 (17)	N2—C5—H5C	109.5
F2—C6—S1	109.46 (18)	H5A—C5—H5C	109.5
C5—N2—C4	112.00 (19)	H5B—C5—H5C	109.5
C5—N2—C1	110.43 (18)	N1—C1—N2	110.71 (18)
C4—N2—C1	111.44 (19)	N1—C1—H1A	109.5
C5—N2—H2	107.0 (17)	N2—C1—H1A	109.5
C4—N2—H2	105.7 (17)	N1—C1—H1B	109.5
C1—N2—H2	110.0 (17)	N2—C1—H1B	109.5
C1—N1—C3	114.3 (2)	H1A—C1—H1B	108.1

O1—S1—N3—S2	138.03 (15)	N3—S2—C7—F4	56.75 (17)
O2—S1—N3—S2	0.3 (2)	O1—S1—C6—F3	176.83 (16)
C6—S1—N3—S2	−112.65 (16)	O2—S1—C6—F3	−58.5 (2)
O3—S2—N3—S1	159.72 (14)	N3—S1—C6—F3	63.3 (2)
O4—S2—N3—S1	22.45 (19)	O1—S1—C6—F1	55.95 (19)
C7—S2—N3—S1	−90.63 (16)	O2—S1—C6—F1	−179.36 (16)
O3—S2—C7—F5	50.34 (18)	N3—S1—C6—F1	−57.55 (19)
O4—S2—C7—F5	175.75 (15)	O1—S1—C6—F2	−64.1 (2)
N3—S2—C7—F5	−62.96 (18)	O2—S1—C6—F2	60.59 (19)
O3—S2—C7—F6	−69.86 (18)	N3—S1—C6—F2	−177.60 (18)
O4—S2—C7—F6	55.55 (19)	C3—N1—C1—N2	97.3 (2)
N3—S2—C7—F6	176.83 (17)	C2—N1—C1—N2	−130.6 (2)
O3—S2—C7—F4	170.06 (16)	C5—N2—C1—N1	−175.3 (2)
O4—S2—C7—F4	−64.54 (18)	C4—N2—C1—N1	59.6 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O4^{i}	0.87 (2)	2.08 (2)	2.868 (3)	150 (2)
N2—H2···O2^{i}	0.87 (2)	2.46 (2)	3.115 (2)	133 (2)
C5—H5*A*···O3^{ii}	0.98	2.38	3.299 (3)	156
C4—H4*C*···O3^{ii}	0.98	2.59	3.444 (3)	145
C5—H5*B*···O1^{iii}	0.98	2.57	3.423 (3)	145

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