IUCrData

ISSN 2414-3146

Poly[1-ethyl-3-methylimidazolium [tri-μ-isothiocyanato-manganate(II)]]

Tim Peppel[a]* and Martin Köckerling[b,c]

[a]Leibniz-Institut für Katalyse e.V., Heterogene Photokatalyse, Albert-Einstein-Str. 29a, D-18059 Rostock, Germany, [b]Universität Rostock, Institut für Chemie, Anorganische Festkörperchemie, Albert-Einstein-Str. 3a, D-18059 Rostock, Germany, and [c]Department Life, Light and Matter, Universität Rostock, 18051 Rostock, Germany. *Correspondence e-mail: tim.peppel@catalysis.de

Received 23 November 2019
Accepted 9 December 2019

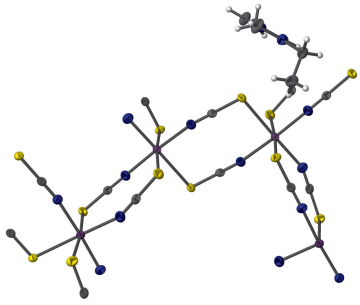
Edited by C. Rizzoli, Universita degli Studi di Parma, Italy

Keywords: manganese; thiocyanate; ionic liquid; crystal structure; network structure.

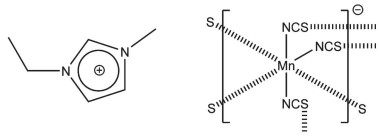
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $\{(C_9H_{11}N_2)[Mn(NCS)_3]\}_n$, has been obtained as a side product of the salt metathesis reaction of 1-ethyl-3-methylimidazolium bromide, (EMIm)Br, and $K_2[Mn(NCS)_4]$. The structure consists of discrete 1-ethyl-3-methylimidazolium cations and an anionic two-dimensional network of manganese(II)-based complex anions, interconnected by thiocyanate ions. Every Mn^{2+} ion is coordinated by three S atoms of three NCS^- ions and three N atoms of further three NCS^- ions in a meridional octahedral fashion.

3D view



Chemical scheme



Structure description

For many years, ionic liquids containing metal ions, especially those with paramagnetic properties have attracted great interest because of their unique properties and possible applications (Santos *et al.*, 2014; Clark *et al.*, 2016). Our ongoing efforts to investigate such low-melting metal-containing ionic liquids were first focused on compounds containing a cobalt ion (Kozlova *et al.*, 2009, Geppert-Rybczyńska *et al.*, 2010; Peppel *et al.*, 2010). Later, Mn containing systems were included (Peppel *et al.*, 2019).

The title compound has been obtained as a side product as a result of a slow chemical decomposition of the ionic liquid $(EMIm)_2[Mn(NCS)_4]$.

Fig. 1 shows the molecular structure of the environment of the Mn^{II} ion, which is coordinated octahedrally by six thiocyanato ligands. Three are N-bonded and the other three S-bonded in a *mer* fashion. All thiocyanato ligands are bridging two Mn ions. Thereby two-dimensional layers are formed. Fig. 2 shows a cutout of the structure of this anionic layer. Whereas the N atoms have almost linear Mn—N—C angles (average of 172.0°), the S atoms are bonded with a Mn—S—C angle of 98.1° (average).

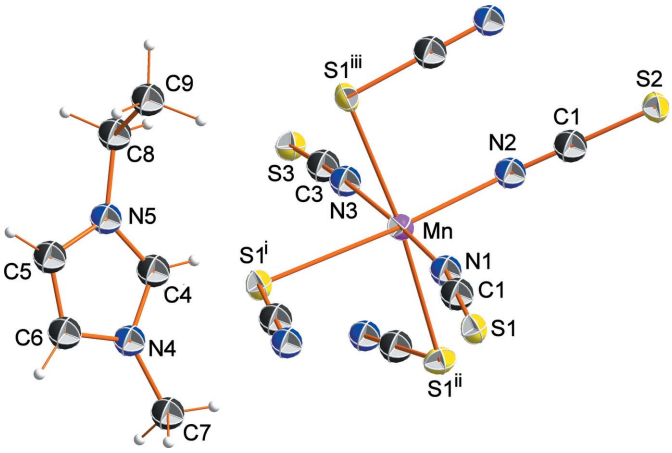


Figure 1
A view of the molecular structure of the octahedrally coordinated $[Mn(NCS)_3(SCN)_3]^-$ units of the polymeric complex anion and the $EMIm^+$ cation of the title compound, with the atoms being presented as 50% displacement ellipsoids. Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $x, \frac{1}{2}-y, -\frac{1}{2}-z$.

The anionic layers are stacked along the crystallographic *a*-axis direction and separated by layers of the $EMIm^+$ cations (see Fig. 3).

A similar type of polymeric structural motive is found in Cd^{II} complexes containing SCN^- ligands (Kuniyasu *et al.*, 1987; Chen *et al.*, 2002; Gao *et al.*, 2008; Dang *et al.*, 2011; Cao *et al.*, 2019).

Synthesis and crystallization

The title compound, $(EMIm)[Mn(NCS)_3]$, was obtained as light-green single crystals directly from a charge of pure, liquid $(EMIm)_2[Mn(NCS)_4]$ over a time period of several months. $(EMIm)_2[Mn(NCS)_4]$ was prepared *via* a salt metathesis reaction from 2.05 mmol of (EMIm)Br (Nishida *et al.*, 2003) and 1.00 mmol of $K_2[Mn(NCS)_4]$ as a light-green liquid in moderate yield (>70%) (Peppel *et al.*, 2019). Elemental analysis for $C_{16}H_{22}MnN_8S_4$ % (calc.): C 37.5 (37.7), H 4.1 (4.3), N 20.6 (21.9), S 22.3 (25.1).

Table 1
Experimental details.

Crystal data	
Chemical formula	$(C_9H_{11}N_2)[Mn(NCS)_3]$
M_r	340.35
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	173
a, b, c (Å)	9.9355 (5), 17.025 (1), 9.7743 (6)
β (°)	116.107 (1)
V (Å^3)	1484.7 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.29
Crystal size (mm)	0.45 × 0.25 × 0.20
Data collection	
Diffractometer	Bruker *APEX* X8 CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2005)
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	20690, 5123, 4084
R_{int}	0.038
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.745
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.065, 1.00
No. of reflections	5123
No. of parameters	207
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.27

Computer programs: *APEX2* and *SAINT* (Bruker, 2005), *SHELXS2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. One low angle reflection (100) was omitted in the structure refinement because its intensity was affected by the beam stop.

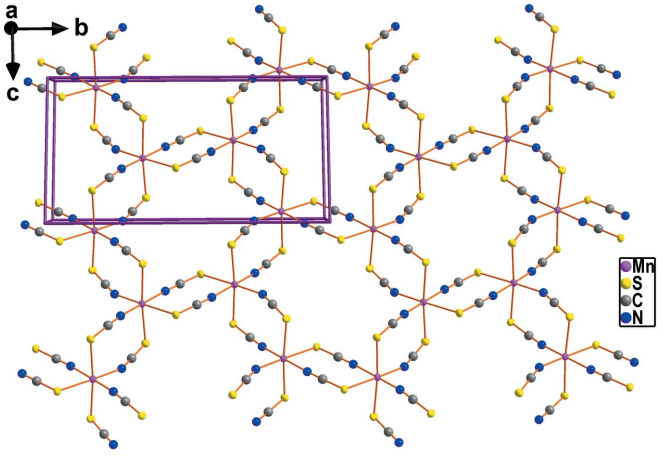


Figure 2
View of the structure of the anionic $[Mn(NCS)_3]^-$ layer.

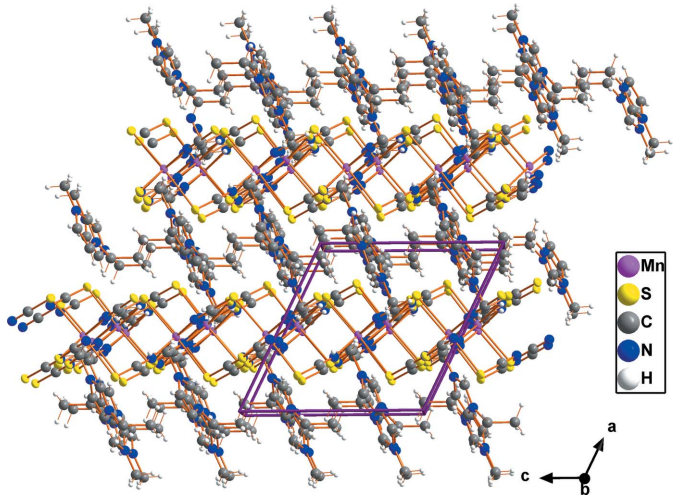


Figure 3
The packing of anionic $[Mn(NCS)_3]^-$ and $EMIM^+$ layers along *a*.

Funding information

Funding for this research was provided by: Deutsche Forschungsgemeinschaft, SPP 1191 (grant No. KO 1616/4-1 und 4-2).

References

Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cao, Y.-J., Zhou, L., Shi, P.-P., Ye, Q. & Fu, D.-W. (2019). *Chem. Commun.* **55**, 8418–8421.
Chen, W., Liu, F. & You, X. (2002). *J. Solid State Chem.* **167**, 119–125.
Clark, K. D., Nacham, O., Purslow, J. A., Pierson, S. A. & Anderson, J. L. (2016). *Anal. Chim. Acta*, **934**, 9–21.
Dang, D.-B., Hu, X.-F., Bai, Y., Qi, Z.-Y. & Yang, F. (2011). *Inorg. Chim. Acta*, **377**, 20–25.
Gao, C., Wu, Y., Gong, H., Hao, X., Xu, X. & Jiang, M. (2008). *Inorg. Chem. Commun.* **11**, 985–987.
Geppert-Rybczyńska, M., Lehmann, J. K., Peppel, T., Köckerling, M. & Heintz, A. (2010). *J. Chem. Eng. Data*, **55**, 5534–5538.
Kozlova, S. A., Verevkin, S. P., Heintz, A., Peppel, T. & Köckerling, M. (2009). *J. Chem. Eng. Data*, **54**, 1524–1528.
Kuniyasu, Y., Suzuki, Y., Taniguchi, M. & Ouchi, A. (1987). *Bull. Chem. Soc. Jpn*, **60**, 179–183.
Nishida, T., Tashiro, Y. & Yamamoto, M. (2003). *J. Fluor. Chem.* **120**, 135–141.
Peppel, T., Geppert-Rybczyńska, M., Neise, C., Kragl, U. & Köckerling, M. (2019). *Materials* **12**, 3764.
Peppel, T., Köckerling, M., Geppert-Rybczyńska, M., Ralys, R. V., Lehmann, J. K., Verevkin, S. P. & Heintz, A. (2010). *Angew. Chem. Int. Ed.* **49**, 7116–7119.
Santos, E., Albo, J. & Irabien, A. (2014). *RSC Adv.* **4**, 40008–40018.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

full crystallographic data

IUCrData (2019). **4**, x191659 [https://doi.org/10.1107/S2414314619016596]

Poly[1-ethyl-3-methylimidazolium [tri-μ-isothiocyanato-manganate(II)]]

Tim Peppel and Martin Köckerling

Poly[1-ethyl-3-methylimidazolium [tri-μ-isothiocyanato-manganate(II)]]

Crystal data

$(C_6H_{11}N_2)[Mn(NCS)_3]$
M_r = 340.35
Monoclinic, $P2_1/c$
a = 9.9355 (5) Å
b = 17.025 (1) Å
c = 9.7743 (6) Å
β = 116.107 (1)°
V = 1484.7 (2) Å^3
Z = 4
$F(000)$ = 692
D_x = 1.523 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5662 reflections
θ = 2.6–31.8°
μ = 1.29 mm^{-1}
T = 173 K
Irregular block, light green
0.45 × 0.25 × 0.20 mm

Data collection

Bruker APEX X8 CCD diffractometer
Radiation source: sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2005)
20690 measured reflections
5123 independent reflections
4084 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 32.0°, θ_{min} = 2.4°
h = −14→14
k = −25→25
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.065
S = 1.00
5123 reflections
207 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2 + 0.2744P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 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. All H atoms were located in a difference Fourier map and refined freely.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn	0.46124 (2)	0.33563 (2)	0.56139 (2)	0.02086 (5)
S1	0.67894 (4)	0.54391 (2)	0.37158 (4)	0.02376 (7)
C1	0.6170 (1)	0.46966 (7)	0.4348 (1)	0.0205 (2)
N1	0.5757 (1)	0.41700 (7)	0.4816 (1)	0.0263 (2)
S2	0.69073 (4)	0.15417 (2)	0.34079 (4)	0.02725 (8)
C2	0.6135 (1)	0.20229 (7)	0.4342 (1)	0.0229 (2)
N2	0.5587 (1)	0.23630 (7)	0.4990 (1)	0.0297 (2)
S3	0.21484 (4)	0.15971 (2)	0.78181 (4)	0.02471 (7)
C3	0.2818 (1)	0.21887 (7)	0.6940 (1)	0.0206 (2)
N3	0.3295 (1)	0.26164 (7)	0.6338 (1)	0.0262 (2)
N4	0.2096 (1)	0.43795 (7)	0.9264 (1)	0.0247 (2)
C4	0.1592 (2)	0.37295 (8)	0.8450 (1)	0.0243 (3)
H4A	0.209 (2)	0.3268 (9)	0.862 (2)	0.029 (4)*
N5	0.0219 (1)	0.38560 (7)	0.7376 (1)	0.0254 (2)
C5	−0.0165 (2)	0.46184 (9)	0.7513 (2)	0.0394 (4)
H5A	−0.108 (2)	0.485 (1)	0.685 (2)	0.058 (6)*
C6	0.1005 (2)	0.4941 (1)	0.8692 (2)	0.0369 (3)
H6A	0.113 (2)	0.542 (1)	0.911 (2)	0.048 (5)*
C7	0.3582 (2)	0.4484 (1)	1.0528 (2)	0.0340 (3)
H7A	0.419 (2)	0.414 (1)	1.052 (2)	0.061 (7)*
H7B	0.351 (2)	0.449 (1)	1.144 (3)	0.069 (7)*
H7C	0.392 (2)	0.496 (1)	1.039 (2)	0.048 (5)*
C8	−0.0702 (2)	0.32934 (9)	0.6187 (2)	0.0290 (3)
H8A	−0.170 (2)	0.3302 (9)	0.610 (2)	0.027 (4)*
H8B	−0.031 (2)	0.2779 (9)	0.653 (2)	0.026 (4)*
C9	−0.0690 (2)	0.3471 (1)	0.4682 (2)	0.0363 (3)
H9A	−0.135 (2)	0.311 (1)	0.395 (2)	0.045 (5)*
H9B	0.035 (2)	0.343 (1)	0.476 (2)	0.047 (5)*
H9C	−0.101 (2)	0.398 (1)	0.441 (2)	0.048 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn	0.0247 (1)	0.01898 (9)	0.02218 (9)	−0.00214 (7)	0.01328 (8)	0.00021 (7)
S1	0.0270 (2)	0.0216 (2)	0.0291 (2)	−0.0018 (1)	0.0182 (1)	0.0014 (1)
C1	0.0178 (5)	0.0237 (6)	0.0211 (5)	0.0019 (5)	0.0095 (5)	−0.0006 (4)
N1	0.0267 (6)	0.0243 (5)	0.0336 (6)	0.0027 (4)	0.0186 (5)	0.0037 (5)
S2	0.0265 (2)	0.0290 (2)	0.0260 (2)	0.0055 (1)	0.0112 (1)	−0.0003 (1)
C2	0.0239 (6)	0.0192 (6)	0.0214 (5)	−0.0007 (5)	0.0061 (5)	0.0017 (4)
N2	0.0347 (6)	0.0271 (6)	0.0258 (5)	0.0037 (5)	0.0119 (5)	−0.0010 (5)
S3	0.0267 (2)	0.0252 (2)	0.0250 (2)	−0.0042 (1)	0.0138 (1)	0.0024 (1)
C3	0.0214 (6)	0.0203 (6)	0.0191 (5)	0.0005 (5)	0.0079 (5)	−0.0018 (4)
N3	0.0288 (6)	0.0263 (6)	0.0231 (5)	−0.0038 (5)	0.0110 (4)	0.0013 (4)
N4	0.0256 (5)	0.0252 (5)	0.0225 (5)	−0.0018 (4)	0.0099 (4)	0.0006 (4)
C4	0.0243 (6)	0.0235 (6)	0.0251 (6)	0.0019 (5)	0.0109 (5)	0.0020 (5)

N5	0.0229 (5)	0.0239 (5)	0.0273 (5)	0.0005 (4)	0.0091 (4)	−0.0022 (4)
C5	0.0337 (8)	0.0302 (8)	0.0414 (8)	0.0109 (6)	0.0047 (7)	−0.0072 (6)
C6	0.0388 (8)	0.0269 (7)	0.0366 (8)	0.0051 (6)	0.0089 (7)	−0.0070 (6)
C7	0.0294 (8)	0.0363 (8)	0.0298 (7)	−0.0072 (7)	0.0073 (6)	−0.0003 (6)
C8	0.0230 (7)	0.0269 (7)	0.0330 (7)	−0.0023 (5)	0.0086 (6)	−0.0057 (6)
C9	0.0337 (8)	0.0393 (9)	0.0347 (8)	−0.0055 (7)	0.0140 (7)	−0.0098 (7)

Geometric parameters (Å, º)

Mn—N1	2.145 (1)	N4—C7	1.460 (2)
Mn—N3	2.149 (1)	C4—N5	1.322 (2)
Mn—N2	2.165 (1)	C4—H4A	0.90 (2)
Mn—S2^{i}	2.6845 (4)	N5—C5	1.376 (2)
Mn—S1^{ii}	2.7163 (4)	N5—C8	1.473 (2)
Mn—S3^{iii}	2.7530 (4)	C5—C6	1.343 (2)
S1—C1	1.641 (1)	C5—H5A	0.94 (2)
S1—Mn^{ii}	2.7163 (4)	C6—H6A	0.89 (2)
C1—N1	1.161 (2)	C7—H7A	0.84 (2)
S2—C2	1.646 (1)	C7—H7B	0.92 (2)
S2—Mn^{iii}	2.6846 (4)	C7—H7C	0.91 (2)
C2—N2	1.156 (2)	C8—C9	1.506 (2)
S3—C3	1.643 (1)	C8—H8A	0.96 (2)
S3—Mn^{i}	2.7530 (4)	C8—H8B	0.96 (2)
C3—N3	1.160 (2)	C9—H9A	0.96 (2)
N4—C4	1.326 (2)	C9—H9B	1.00 (2)
N4—C6	1.367 (2)	C9—H9C	0.93 (2)
N1—Mn—N3	174.68 (4)	N4—C4—H4A	126 (1)
N1—Mn—N2	91.59 (4)	C4—N5—C5	108.0 (1)
N3—Mn—N2	92.73 (5)	C4—N5—C8	125.9 (1)
N1—Mn—S2^{i}	88.82 (3)	C5—N5—C8	126.0 (1)
N3—Mn—S2^{i}	94.04 (3)	C6—C5—N5	107.3 (1)
N2—Mn—S2^{i}	92.99 (3)	C6—C5—H5A	129 (1)
N1—Mn—S1^{ii}	90.58 (3)	N5—C5—H5A	124 (1)
N3—Mn—S1^{ii}	84.94 (3)	C5—C6—N4	107.2 (1)
N2—Mn—S1^{ii}	176.25 (3)	C5—C6—H6A	131 (1)
S2^{i}—Mn—S1^{ii}	90.11 (1)	N4—C6—H6A	122 (1)
N1—Mn—S3^{iii}	90.14 (3)	N4—C7—H7A	112 (1)
N3—Mn—S3^{iii}	86.53 (3)	N4—C7—H7B	110 (1)
N2—Mn—S3^{iii}	93.18 (3)	H7A—C7—H7B	112 (2)
S2^{i}—Mn—S3^{iii}	173.77 (1)	N4—C7—H7C	106 (1)
S1^{ii}—Mn—S3^{iii}	83.76 (1)	H7A—C7—H7C	108 (2)
C1—S1—Mn^{ii}	100.02 (4)	H7B—C7—H7C	109 (2)
N1—C1—S1	178.8 (1)	N5—C8—C9	111.8 (1)
C1—N1—Mn	168.1 (1)	N5—C8—H8A	108.5 (9)
C2—S2—Mn^{iii}	97.91 (5)	C9—C8—H8A	111.5 (9)
N2—C2—S2	179.6 (1)	N5—C8—H8B	107.5 (9)
C2—N2—Mn	157.2 (1)	C9—C8—H8B	110.7 (9)

C3—S3—Mn^{i}	96.51 (4)	H8A—C8—H8B	107 (1)
N3—C3—S3	178.8 (1)	C8—C9—H9A	108 (1)
C3—N3—Mn	168.2 (1)	C8—C9—H9B	111 (1)
C4—N4—C6	108.4 (1)	H9A—C9—H9B	111 (2)
C4—N4—C7	125.7 (1)	C8—C9—H9C	109 (1)
C6—N4—C7	125.8 (1)	H9A—C9—H9C	111 (2)
N5—C4—N4	109.0 (1)	H9B—C9—H9C	107 (2)
N5—C4—H4A	125 (1)		

C6—N4—C4—N5	0.1 (2)	N5—C5—C6—N4	0.3 (2)
C7—N4—C4—N5	−178.2 (1)	C4—N4—C6—C5	−0.2 (2)
N4—C4—N5—C5	0.1 (2)	C7—N4—C6—C5	178.0 (1)
N4—C4—N5—C8	176.8 (1)	C4—N5—C8—C9	−100.8 (2)
C4—N5—C5—C6	−0.2 (2)	C5—N5—C8—C9	75.3 (2)
C8—N5—C5—C6	−176.9 (1)		

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