



Crystal structure of the co-crystal *fac*-triaquatis-(thiocyanato- κ N)iron(III)–2,3-dimethylpyrazine (1/3)

Olesia I. Kucheriv,^{a*} Sergii I. Shylin,^a Tetiana A. Ilina,^b Sebastian Dechert^c and Il'ya A. Gural'skiy^a

Received 3 March 2015

Accepted 9 March 2015

Edited by D.-J. Xu, Zhejiang University (Yuquan Campus), China

^aDepartment of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska st. 64, Kyiv 01601, Ukraine, ^bKherson National Technical University, Beryslavske st. 24, Kherson 73008, Ukraine, and ^cInstitute of Inorganic Chemistry, Georg-August-University Göttingen, Tammannstrasse 4, Göttingen D-37077, Germany. *Correspondence e-mail: lesya.kucheriv@gmail.com

Keywords: crystal structure; Fe^{III} complex; iso-thiocyanate ligand; pyrazine; co-crystal; hydrogen bonding

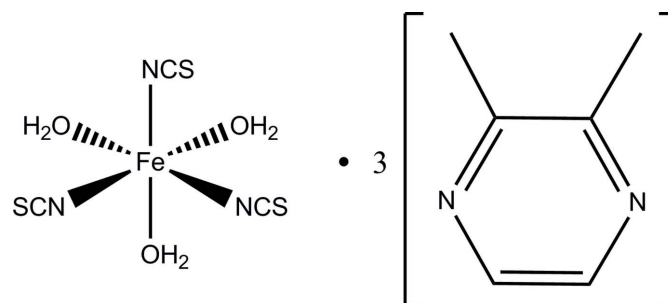
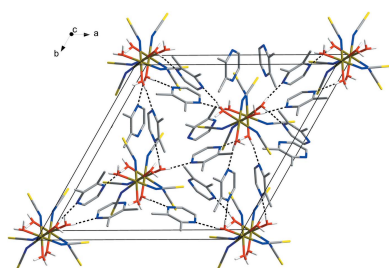
CCDC reference: 1053032

Supporting information: this article has supporting information at journals.iucr.org/e

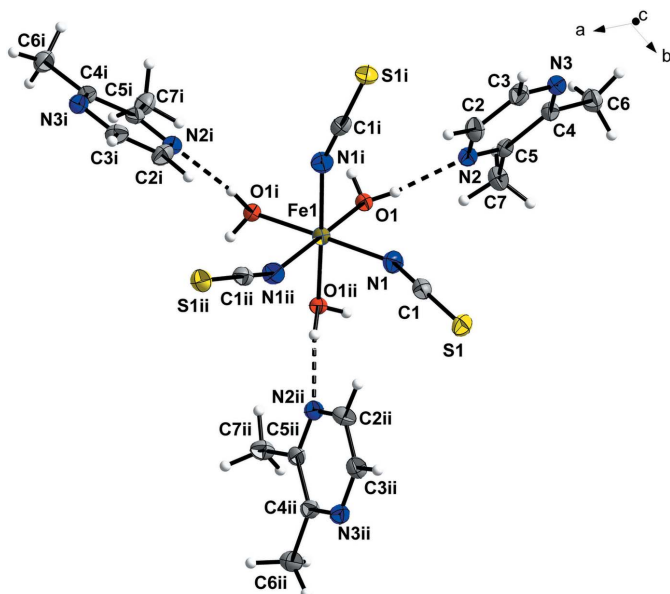
In the crystal of the title compound, [Fe(NCS)₃(H₂O)₃]:3C₆H₈N₂, the Fe^{III} cation is located on a threefold rotation axis and is coordinated by three N atoms of the thiocyanate anions and three water molecules in a *fac* arrangement, forming a slightly distorted N₃O₃ octahedron. Stabilization within the crystal structure is provided by O–H···N hydrogen bonds; the H atoms from coordinating water molecules act as donors to the N atoms of guest 2,3-dimethylpyrazine molecules, leading to a three-dimensional supramolecular framework.

1. Chemical context

In the large family of coordination compounds, materials showing a tunable character of their physical properties (*e.g.*, electrical, magnetic, optical *etc*) are of special interest. Attempts to design compounds with such tunability have revealed the possibility to target the property of interest through the rational choice of ligands in transition metal complexes. For instance, variation of the aromatic *N*-donor ligand can lead to possible spin-state modulation of transition metals. In certain cases, these complexes can even possess spin crossover behaviour (transition between low and high spin states of a metal). The phenomenon of spin transition, which is one of the most known examples of molecular bistability, can be provoked by some external stimuli (temperature, pressure, light, magnetic field, absorption of some compounds) and is followed by a change of the optical, magnetic and electric properties (Gütlich & Goodwin, 2004).

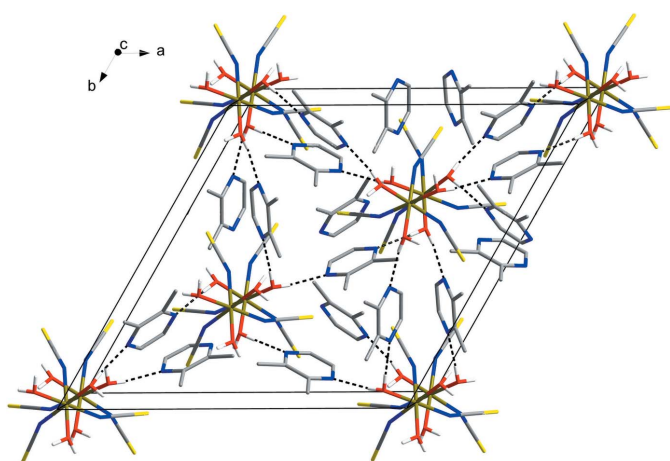


One of the simplest bridging *N*-donor ligands in the design of coordination polymers is pyrazine. This ligand is known for the formation of not only low-dimensional chains and sheets but also of some more complicated architectures, such as [Ag(pz)](CB₁₁H₁₂) [CB₁₁H₁₂[−] is the monocarba-*closo*-


Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-y + 1, x - y + 1, z$; (ii) $-x + y, -x + 1, z$.]

dodecaborate(−) anion], which exhibits a three-dimensional structure made up of checkerboard sheets of silver cations and anions connected by pillars of bridging pyrazine ligands (Cunha-Silva *et al.*, 2006). In addition, pyrazine is able to construct Hofmann clathrates – spin crossover compounds with general formula $[\text{Fe}^{\text{II}}\text{M}^{\text{II}}(\text{pz})(\text{CN})_4]_{\infty}$ where $M = \text{Ni}, \text{Pd}$ or Pt (Niel *et al.*, 2001). A combination of pyrazine ligands with thiocyanates instead of tetracyanidometalates leads to the two-dimensional coordination polymer $[\text{Fe}(\text{pz})_2(\text{NCS})_2]_{\infty}$ with an antiferromagnetic exchange between the metal cations (Real *et al.*, 1991). In this context, we attempted to synthesize an Fe^{II} thiocyanate complex with 2,3-dimethylpyrazine;


Figure 2

Crystal structure of the title compound, showing hydrogen bonds as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity. Colour key: bronze Fe, yellow S, blue N, grey C and red O.

Table 1

Hydrogen-bond geometry ($\text{\AA}, ^{\circ}$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1A}\cdots\text{N2}$	0.80 (3)	1.95 (3)	2.745 (4)	172 (8)

however, the exposure of the starting material $[\text{Fe}(\text{OTs})_2]\cdot 6\text{H}_2\text{O}$ ($\text{OTs} = p\text{-toluenesulfonate}$) to the oxygen in the air led to the oxidation of Fe^{II} and to the formation of the title compound.

2. Structural commentary

In the crystal structure of the title compound, the Fe^{III} cation is located on a threefold rotation axis and is in an octahedral coordination environment formed by three N atoms of the thiocyanate anions and three O atoms of water molecules arranged in a *fac* configuration (Fig. 1). The distance between the Fe^{III} ion and the N atoms [2.025 (4) \AA] is longer than that between the Fe^{III} ion and the O atoms [2.034 (3) \AA] and therefore the FeN_3O_3 octahedron is slightly distorted. These structural features are typical for related compounds (Shylin *et al.*, 2013, 2015). The thiocyanate ligands are bound through

Table 2

Experimental details.

Crystal data	
Chemical formula	$[\text{Fe}(\text{NCS})_3(\text{H}_2\text{O})_3]\cdot 3\text{C}_6\text{H}_8\text{N}_2$
M_r	608.57
Crystal system, space group	Trigonal, $R3c$
Temperature (K)	133
a, c (\AA)	16.9383 (12), 17.6259 (13)
V (\AA^3)	4379.5 (7)
Z	6
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.77
Crystal size (mm)	$0.16 \times 0.12 \times 0.1$
Data collection	
Diffractometer	Stoe IPDS II
Absorption correction	Numerical ($X\text{-RED}$; Stoe & Cie, 2002)
$T_{\text{min}}, T_{\text{max}}$	0.908, 0.939
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5784, 1903, 1716
R_{int}	0.058
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.633
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.070, 1.07
No. of reflections	1903
No. of parameters	120
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e \AA^{-3})	0.27, −0.28
Absolute structure	Flack x determined using 685 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	−0.03 (3)

Computer programs: $X\text{-AREA}$ and $X\text{-RED}$ (Stoe & Cie, 2002), $SHELXS97$ (Sheldrick, 2008), $SHELXL2014$ (Sheldrick, 2015), $OLEX2$ (Dolomanov *et al.*, 2009) and $publCIF$ (Westrip, 2010).

nitrogen atoms and are quasi-linear [$\text{N1}-\text{C1}-\text{S1} = 179.5(4)^\circ$], while the Fe–NCS linkages are bent [$\text{C1}-\text{N1}-\text{Fe1} = 157.0(4)^\circ$]. Previously reported complexes with an N-bound NCS group possess similar structural features (Petrusenko *et al.*, 1997).

3. Supramolecular features

In the title compound, the crystal packing is stabilized by O–H···N hydrogen bonds (Table 1): the H atoms from coordinating water molecules act as donors to the N atoms of guest 2,3-dimethylpyrazine molecules. The compound contains three guest molecules of pyrazine per Fe^{III} cation. In the crystal lattice, each molecule of the complex is attached to six molecules of pyrazine, while each pyrazine is connected with two water molecules of the host complexes, leading to the formation of a three-dimensional network (Fig. 2).

4. Synthesis and crystallization

Crystals of the title compound were obtained by the slow-diffusion method between three layers, the first layer being a solution of $[\text{Fe}(\text{OTs})_2] \cdot 6\text{H}_2\text{O}$ (0.096 g, 0.2 mmol) and NH_4SCN (0.046 g, 0.6 mmol) in water (10 ml), the second being a water/methanol mixture (1/1, 10 ml) and the third a solution of 2,3-dimethylpyrazine (0.065 g, 0.6 mmol) in methanol (3 ml). After two weeks, red plates grew in the second layer; they were collected, washed with water and dried in air, yield 0.028 g (23%).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms connected to

C and O atoms were placed in their expected calculated positions and refined as riding with $\text{C}-\text{H} = 0.98$ (CH_3), 0.95 (C_{arom}), $\text{O}-\text{H} = 0.80$ (3) Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$ with the exception of methyl hydrogen atoms, which were refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

Acknowledgements

SIS and IAG acknowledge DAAD fellowships and the hosting of Professor F. Meyer's group.

References

- Cunha-Silva, L., Ahmad, R. & Hardie, M. J. (2006). *Aust. J. Chem.* **59**, 40–48.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Gütlich, P. & Goodwin, H. (2004). *Spin Crossover in Transition Metal Compounds I*, pp. 1–47. Berlin, Heidelberg: Springer-Verlag.
- Niel, V., Martinez-Agudo, J. M., Muñoz, M. C., Gaspar, A. B. & Real, J. A. (2001). *Inorg. Chem.* **40**, 3838–3839.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Petrusenko, S. R., Kokozay, V. N. & Fritsky, I. O. (1997). *Polyhedron*, **16**, 267–274.
- Real, J. A., De Munno, G., Munoz, M. C. & Julve, M. (1991). *Inorg. Chem.* **30**, 2701–2704.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Shylin, S. I., Gural'skiy, I. A., Bykov, D., Demeshko, S., Dechert, S., Meyer, F., Hauka, M. & Fritsky, I. O. (2015). *Polyhedron*, **87**, 147–155.
- Shylin, S. I., Gural'skiy, I. A., Hauka, M. & Golenya, I. A. (2013). *Acta Cryst.* **E69**, m280.
- Stoe & Cie (2002). *X-RED* and *X-AREA*. Stoe & Cie, Darmstadt, Germany.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2015). E71, 374-376 [doi:10.1107/S2056989015004831]

Crystal structure of the co-crystal *fac*-triaquatis(thiocyanato- κ N)iron(III)–2,3-dimethylpyrazine (1/3)

Olesia I. Kucheriv, Sergii I. Shylin, Tetiana A. Ilina, Sebastian Dechert and Il'ya A. Gural'skiy

Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

fac-Triaquatis(thiocyanato- κ N)iron(III)–2,3-dimethylpyrazine (1/3)

Crystal data

[Fe(NCS)₃(H₂O)₃]:3C₆H₈N₂

$M_r = 608.57$

Trigonal, *R3c*

$a = 16.9383$ (12) Å

$c = 17.6259$ (13) Å

$V = 4379.5$ (7) Å³

$Z = 6$

$F(000) = 1902$

$D_x = 1.384$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

$\mu = 0.77$ mm⁻¹

$T = 133$ K

Block, red

0.16 × 0.12 × 0.1 mm

Data collection

Stoe IPDS II

diffractometer

φ scans and ω scans with κ offset

Absorption correction: numerical
(X-RED; Stoe & Cie, 2002)

$T_{\min} = 0.908$, $T_{\max} = 0.939$

5784 measured reflections

1903 independent reflections

1716 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$

$\theta_{\max} = 26.8^\circ$, $\theta_{\min} = 2.4^\circ$

$h = -18 \rightarrow 21$

$k = -21 \rightarrow 15$

$l = -18 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.070$

$S = 1.07$

1903 reflections

120 parameters

3 restraints

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

$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.27$ e Å⁻³

$\Delta\rho_{\min} = -0.28$ e Å⁻³

Absolute structure: Flack x determined using
685 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*,
2013)

Absolute structure parameter: -0.03 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.3333	0.6667	0.99891 (7)	0.0201 (2)
S1	0.29300 (8)	0.86373 (8)	1.16318 (7)	0.0300 (3)
N1	0.2860 (3)	0.7347 (3)	1.0611 (2)	0.0297 (9)
O1	0.2256 (2)	0.62277 (19)	0.92686 (19)	0.0221 (6)
C1	0.2893 (3)	0.7891 (3)	1.1041 (3)	0.0238 (9)
N2	0.0562 (2)	0.5854 (2)	0.9750 (2)	0.0250 (8)
N3	-0.1220 (2)	0.5016 (2)	1.0276 (2)	0.0254 (8)
C2	0.0336 (3)	0.5471 (3)	1.0439 (3)	0.0299 (10)
H2	0.0796	0.5481	1.0753	0.036*
C3	-0.0543 (3)	0.5064 (3)	1.0704 (3)	0.0288 (10)
H3	-0.0674	0.4812	1.1201	0.035*
C4	-0.1008 (3)	0.5385 (3)	0.9586 (2)	0.0235 (9)
C5	-0.0099 (3)	0.5815 (3)	0.9318 (3)	0.0229 (9)
C6	-0.1766 (3)	0.5322 (3)	0.9107 (3)	0.0322 (10)
H6A	-0.2345	0.4977	0.9379	0.048*
H6B	-0.1795	0.5010	0.8630	0.048*
H6C	-0.1655	0.5936	0.8996	0.048*
C7	0.0144 (3)	0.6246 (3)	0.8553 (3)	0.0304 (10)
H7A	0.0795	0.6484	0.8459	0.046*
H7B	0.0012	0.6747	0.8531	0.046*
H7C	-0.0214	0.5791	0.8166	0.046*
H1A	0.179 (3)	0.617 (5)	0.943 (4)	0.080*
H1B	0.206 (5)	0.572 (3)	0.912 (4)	0.080*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0197 (3)	0.0197 (3)	0.0209 (5)	0.00986 (13)	0.000	0.000
S1	0.0320 (6)	0.0293 (5)	0.0316 (6)	0.0175 (5)	0.0009 (5)	-0.0061 (5)
N1	0.030 (2)	0.031 (2)	0.029 (2)	0.0157 (18)	0.0031 (17)	-0.0024 (18)
O1	0.0180 (14)	0.0201 (14)	0.0283 (17)	0.0096 (13)	-0.0011 (13)	-0.0021 (13)
C1	0.022 (2)	0.030 (2)	0.022 (2)	0.0141 (18)	0.0019 (17)	0.0053 (18)
N2	0.0234 (18)	0.0234 (17)	0.028 (2)	0.0119 (15)	-0.0004 (16)	-0.0026 (15)
N3	0.0236 (17)	0.0233 (17)	0.029 (2)	0.0113 (15)	0.0027 (15)	0.0001 (15)
C2	0.027 (2)	0.037 (2)	0.030 (3)	0.019 (2)	-0.0040 (19)	-0.001 (2)
C3	0.032 (2)	0.029 (2)	0.028 (3)	0.018 (2)	0.0022 (19)	0.0030 (19)
C4	0.021 (2)	0.023 (2)	0.027 (2)	0.0113 (16)	0.0008 (18)	-0.0022 (18)
C5	0.023 (2)	0.0203 (19)	0.027 (2)	0.0121 (17)	0.0023 (17)	-0.0028 (17)
C6	0.027 (2)	0.036 (3)	0.035 (3)	0.017 (2)	-0.002 (2)	-0.002 (2)

C7	0.026 (2)	0.037 (2)	0.028 (3)	0.016 (2)	0.0020 (19)	0.0020 (19)
----	-----------	-----------	-----------	-----------	-------------	-------------

Geometric parameters (Å, °)

Fe1—N1	2.025 (4)	N3—C4	1.333 (6)
Fe1—N1 ⁱ	2.025 (4)	C2—H2	0.9500
Fe1—N1 ⁱⁱ	2.025 (4)	C2—C3	1.372 (6)
Fe1—O1	2.034 (3)	C3—H3	0.9500
Fe1—O1 ⁱ	2.034 (3)	C4—C5	1.415 (6)
Fe1—O1 ⁱⁱ	2.034 (3)	C4—C6	1.495 (6)
S1—C1	1.615 (5)	C5—C7	1.491 (6)
N1—C1	1.172 (6)	C6—H6A	0.9800
O1—H1A	0.80 (3)	C6—H6B	0.9800
O1—H1B	0.80 (3)	C6—H6C	0.9800
N2—C2	1.339 (6)	C7—H7A	0.9800
N2—C5	1.329 (5)	C7—H7B	0.9800
N3—C3	1.340 (6)	C7—H7C	0.9800
N1—Fe1—N1 ⁱ	93.42 (17)	N2—C2—C3	121.9 (4)
N1—Fe1—N1 ⁱⁱ	93.42 (17)	C3—C2—H2	119.0
N1 ⁱ —Fe1—N1 ⁱⁱ	93.42 (16)	N3—C3—C2	121.2 (5)
N1—Fe1—O1 ⁱⁱ	90.67 (14)	N3—C3—H3	119.4
N1 ⁱⁱ —Fe1—O1 ⁱⁱ	90.47 (14)	C2—C3—H3	119.4
N1 ⁱⁱ —Fe1—O1 ⁱ	90.67 (14)	N3—C4—C5	120.9 (4)
N1 ⁱ —Fe1—O1 ⁱⁱ	174.17 (17)	N3—C4—C6	117.6 (4)
N1—Fe1—O1	90.47 (14)	C5—C4—C6	121.5 (4)
N1 ⁱ —Fe1—O1 ⁱ	90.47 (14)	N2—C5—C4	120.5 (4)
N1 ⁱⁱ —Fe1—O1	174.17 (17)	N2—C5—C7	118.3 (4)
N1 ⁱ —Fe1—O1	90.67 (14)	C4—C5—C7	121.2 (4)
N1—Fe1—O1 ⁱ	174.17 (17)	C4—C6—H6A	109.5
O1—Fe1—O1 ⁱⁱ	85.15 (14)	C4—C6—H6B	109.5
O1 ⁱⁱ —Fe1—O1 ⁱ	85.15 (14)	C4—C6—H6C	109.5
O1—Fe1—O1 ⁱ	85.15 (14)	H6A—C6—H6B	109.5
C1—N1—Fe1	157.0 (4)	H6A—C6—H6C	109.5
Fe1—O1—H1A	118 (6)	H6B—C6—H6C	109.5
Fe1—O1—H1B	115 (6)	C5—C7—H7A	109.5
H1A—O1—H1B	98 (7)	C5—C7—H7B	109.5
N1—C1—S1	179.5 (4)	C5—C7—H7C	109.5
C5—N2—C2	117.7 (4)	H7A—C7—H7B	109.5
C4—N3—C3	117.7 (4)	H7A—C7—H7C	109.5
N2—C2—H2	119.0	H7B—C7—H7C	109.5
N2—C2—C3—N3	1.5 (7)	C3—N3—C4—C6	179.4 (4)
N3—C4—C5—N2	0.4 (6)	C4—N3—C3—C2	-0.7 (7)
N3—C4—C5—C7	-178.7 (4)	C5—N2—C2—C3	-1.2 (6)
C2—N2—C5—C4	0.3 (6)	C6—C4—C5—N2	-179.2 (4)

C2—N2—C5—C7	179.5 (4)	C6—C4—C5—C7	1.7 (6)
C3—N3—C4—C5	-0.2 (6)		

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1—H1A...N2	0.80 (3)	1.95 (3)	2.745 (4)	172 (8)
