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Crystal structure of tetraaquabis(thiocyanato-κN)nickel(II)–2,5-dimethylpyrazine (1/4)

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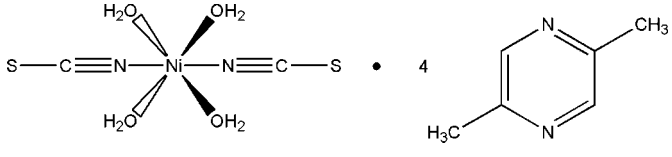
In the crystal structure of the title compound, $[Ni(NCS)_2(H_2O)_4]\cdot 4C_6H_8N_2$, the Ni^{II} cations are coordinated by four water ligands and two *trans*-coordinated terminally *N*-bonded thiocyanate anions in a slightly distorted octahedral geometry. The asymmetric unit consists of a Ni^{2+} cation located on a centre of inversion, two water molecules and one thiocyanate ligand, as well as two uncoordinated 2,5-dimethylpyrazine ligands in general positions. In the crystal, discrete complex molecules are linked into a three-dimensional network by O—H···N hydrogen bonding between the water H atoms and the 2,5-dimethylpyrazine N atoms.

Keywords: crystal structure; thiocyanat; nickel(II) complex; 2,5-dimethylpyrazine; hydrogen bonding.

CCDC reference: 1038309

1. Related literature

For background information on the design and preparation of coordination polymers, see Näther *et al.* (2013). For a different structure with thiocyanates and 2,5-dimethylpyrazine, see: Otieno *et al.* (2003).



2. Experimental

2.1. Crystal data

$[Ni(NCS)_2(H_2O)_4]\cdot 4C_6H_8N_2$
M_r = 679.51
Orthorhombic, *Pbca*
a = 13.0731 (6) Å
b = 14.7989 (8) Å
c = 17.3092 (11) Å
V = 3348.8 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.75 mm^{-1}
T = 170 K
0.12 × 0.10 × 0.08 mm

2.2. Data collection

Stoe IPDS-1 diffractometer
Absorption correction: numerical (*X-SHAPE* and *X-RED32*; Stoe & Cie, 2008)
T_{min} = 0.912, T_{max} = 0.938
21266 measured reflections
4041 independent reflections
3146 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.100
S = 1.02
4041 reflections
201 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O*1···N12	0.84	1.99	2.8284 (18)	174
O1—H2*O*1···N11^{i}	0.84	2.06	2.8963 (18)	173
O2—H1*O*2···N2^{ii}	0.84	2.00	2.8286 (19)	169
O2—H2*O*2···N1^{iii}	0.84	2.03	2.8665 (19)	176

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

Data collection: *X-AREA* (Stoe & Cie, 2008); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: PK2540).

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supporting information

Acta Cryst. (2015). E**71**, m18 [doi:10.1107/S2056989014026991]

Crystal structure of tetraaquabis(thiocyanato-κN)nickel(II)–2,5-dimethylpyrazine (1/4)

Stefan Suckert, Mario Wriedt, Inke Jess and Christian Näther

S1. Synthesis and crystallization

$NiSO_4.6\ H_2O$ and 2,5-dimethylpyrazine were purchased from Merck and $Ba(NCS)_2.3\ H_2O$ was purchased from Alfa Aesar. $Ni(NCS)_2$ was synthesized by stirring 17.5 g (56.91 mmol) $Ba(NCS)_2.3\ H_2O$ and 15.00 g (57.03 mmol) $NiSO_4.6\ H_2O$ in 500 ml H_2O at RT for two hours. The white residue of $BaSO_4$ was filtered of and the solvent removed with a rotary evaporator. The homogeneity of the product was investigated by X-ray powder diffraction and elemental analysis. The title compound was prepared by the reaction of (0.15 mmol) 27.8 mg $Ni(NCS)_2$ and (0.9 mmol) 97.5 μl 2,5-dimethylpyrazine at RT. After a few days blue block shaped crystals of the title compound were obtained.

S2. Refinement

The C—H H atoms were positioned with idealized geometry (methyl H atoms allowed to rotate but not to tip) and were refined using a riding model with C—H = 0.95 Å for aromatic and C—H = 0.98 Å for methyl. Water hydrogen atoms were found in difference-electron density maps and fixed (SHELXL command AFIX 3). U_{iso}(H) values were set to either $1.2U_{eq}$ or $1.5U_{eq}$ (-CH_3, H_2O) of the attached parent atom.

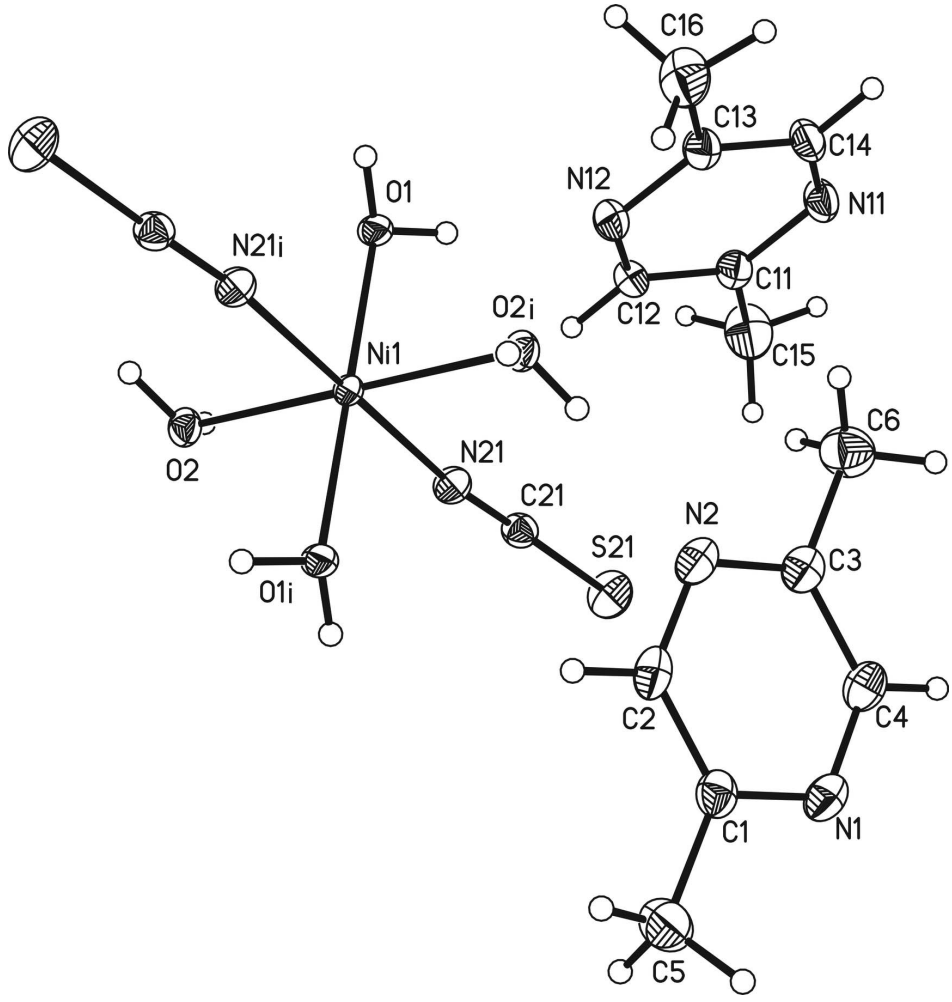

Figure 1

Part of the crystal structure of the title compound with labelling and displacement ellipsoids drawn at the 50% probability level. Symmetry code: i = x+1,-y+1,-z+1.

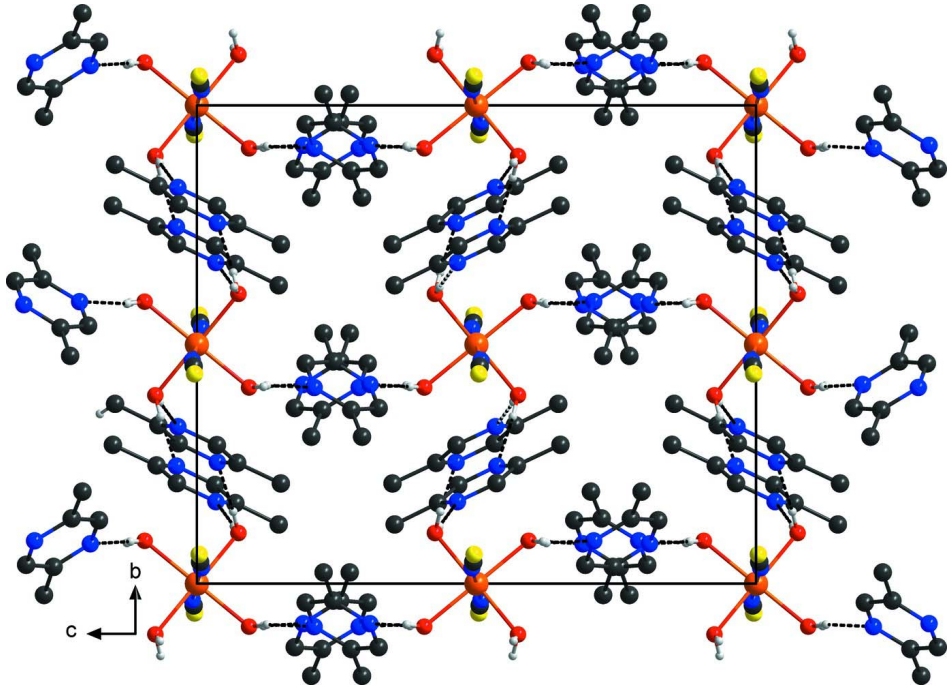

Figure 2

Crystal structure of the title compound with view along the crystallographic *a* axis. Hydrogen bonding is shown as dashed lines and for clarity only the O-H H atoms are shown.

Tetraaquabis(thiocyanato-*κN*)nickel(II)–2,5-dimethylpyrazine (1/4)

Crystal data

$[Ni(NCS)_2(H_2O)_4]\cdot 4C_6H_8N_2$
$M_r = 679.51$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
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$b = 14.7989\ (8)$ Å
$c = 17.3092\ (11)$ Å
$V = 3348.8\ (3)$ Å^3
$Z = 4$
$F(000) = 1432$
$D_x = 1.348$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 21266 reflections
$\theta = 2.8–28.1°$
$\mu = 0.75$ mm^{-1}
$T = 170$ K
Block, blue
0.12 × 0.10 × 0.08 mm

Data collection

Stoe IPDS-1 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ scans
Absorption correction: numerical (*X-SHAPE* and *X-RED32*; Stoe & Cie, 2008)
$T_{min} = 0.912$, $T_{max} = 0.938$
21266 measured reflections
4041 independent reflections
3146 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 28.1°$, $\theta_{min} = 2.8°$
$h = -17\rightarrow15$
$k = -19\rightarrow19$
$l = -22\rightarrow22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.100$
$S = 1.02$
4041 reflections
201 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 0.7837P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Extinction coefficient: 0.0068 (8)

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 $F^2 > 2$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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.5000	0.5000	0.5000	0.01215 (11)
N21	0.34876 (11)	0.53353 (10)	0.50818 (8)	0.0178 (3)
C21	0.26112 (13)	0.54542 (11)	0.50572 (8)	0.0161 (3)
S21	0.13689 (3)	0.56120 (4)	0.50416 (3)	0.02775 (13)
O1	0.51049 (8)	0.58972 (8)	0.40668 (6)	0.0160 (2)
H1O1	0.4561	0.5882	0.3809	0.024*
H2O1	0.5589	0.5854	0.3750	0.024*
O2	0.54012 (9)	0.60597 (8)	0.57432 (6)	0.0162 (2)
H1O2	0.6015	0.6200	0.5663	0.024*
H2O2	0.5025	0.6507	0.5650	0.024*
N1	0.09222 (12)	0.25396 (10)	0.53656 (9)	0.0231 (3)
N2	0.26379 (12)	0.32843 (10)	0.46598 (9)	0.0223 (3)
C1	0.18340 (14)	0.25266 (11)	0.57207 (10)	0.0211 (3)
C2	0.26824 (14)	0.28976 (12)	0.53578 (11)	0.0227 (4)
H2	0.3323	0.2876	0.5616	0.027*
C3	0.17233 (14)	0.33146 (11)	0.43120 (10)	0.0210 (3)
C4	0.08758 (14)	0.29358 (12)	0.46734 (11)	0.0235 (4)
H4	0.0234	0.2960	0.4416	0.028*
C5	0.18951 (17)	0.20962 (14)	0.65016 (11)	0.0321 (4)
H5A	0.1634	0.2517	0.6892	0.048*
H5B	0.2609	0.1947	0.6618	0.048*
H5C	0.1483	0.1543	0.6506	0.048*
C6	0.16595 (17)	0.37609 (14)	0.35372 (11)	0.0328 (4)

H6A	0.1624	0.4418	0.3605	0.049*
H6B	0.1045	0.3551	0.3267	0.049*
H6C	0.2267	0.3606	0.3233	0.049*
N11	0.16959 (11)	0.58969 (10)	0.20976 (8)	0.0228 (3)
N12	0.33677 (12)	0.58344 (10)	0.30944 (8)	0.0211 (3)
C11	0.16897 (13)	0.63643 (11)	0.27609 (10)	0.0208 (3)
C12	0.25374 (14)	0.63271 (12)	0.32501 (9)	0.0203 (3)
H12	0.2523	0.6668	0.3715	0.024*
C13	0.33614 (14)	0.53519 (12)	0.24377 (10)	0.0207 (3)
C14	0.25231 (14)	0.53952 (13)	0.19461 (10)	0.0225 (4)
H14	0.2538	0.5053	0.1482	0.027*
C15	0.07737 (16)	0.69264 (15)	0.29538 (13)	0.0374 (5)
H15A	0.0305	0.6935	0.2512	0.056*
H15B	0.0992	0.7545	0.3072	0.056*
H15C	0.0424	0.6668	0.3403	0.056*
C16	0.42685 (16)	0.47645 (15)	0.22664 (13)	0.0332 (4)
H16A	0.4875	0.5144	0.2194	0.050*
H16B	0.4140	0.4417	0.1795	0.050*
H16C	0.4383	0.4349	0.2699	0.050*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.00735 (16)	0.01786 (16)	0.01122 (15)	0.00033 (10)	−0.00024 (9)	0.00008 (10)
N21	0.0123 (7)	0.0226 (7)	0.0185 (7)	0.0012 (5)	0.0013 (5)	−0.0007 (5)
C21	0.0155 (8)	0.0178 (8)	0.0150 (7)	0.0015 (6)	0.0008 (6)	−0.0004 (6)
S21	0.0102 (2)	0.0405 (3)	0.0326 (3)	0.00601 (18)	−0.00014 (16)	−0.00175 (19)
O1	0.0108 (5)	0.0242 (6)	0.0131 (5)	−0.0002 (4)	0.0000 (4)	0.0033 (4)
O2	0.0121 (5)	0.0196 (5)	0.0170 (5)	0.0007 (4)	−0.0014 (4)	−0.0024 (4)
N1	0.0170 (7)	0.0221 (7)	0.0300 (8)	−0.0023 (6)	0.0024 (6)	−0.0015 (6)
N2	0.0178 (7)	0.0197 (7)	0.0293 (7)	−0.0027 (6)	0.0026 (6)	−0.0032 (6)
C1	0.0228 (8)	0.0178 (7)	0.0228 (8)	−0.0007 (7)	−0.0004 (6)	−0.0046 (6)
C2	0.0167 (8)	0.0225 (8)	0.0291 (9)	−0.0016 (7)	−0.0039 (7)	−0.0045 (7)
C3	0.0196 (8)	0.0171 (7)	0.0262 (8)	0.0017 (7)	0.0014 (7)	−0.0031 (6)
C4	0.0149 (8)	0.0251 (8)	0.0306 (9)	0.0005 (7)	−0.0018 (7)	0.0001 (7)
C5	0.0392 (12)	0.0327 (10)	0.0245 (9)	−0.0022 (9)	−0.0025 (8)	0.0009 (7)
C6	0.0359 (11)	0.0327 (10)	0.0298 (10)	0.0014 (9)	−0.0009 (8)	0.0057 (8)
N11	0.0184 (7)	0.0299 (8)	0.0201 (7)	0.0006 (6)	−0.0050 (6)	−0.0042 (6)
N12	0.0207 (7)	0.0256 (7)	0.0170 (6)	−0.0020 (6)	−0.0046 (5)	0.0009 (5)
C11	0.0189 (8)	0.0226 (8)	0.0209 (8)	−0.0012 (7)	−0.0006 (6)	−0.0015 (6)
C12	0.0226 (8)	0.0234 (8)	0.0151 (7)	−0.0032 (7)	−0.0009 (6)	−0.0023 (6)
C13	0.0184 (8)	0.0241 (8)	0.0198 (8)	−0.0004 (7)	−0.0023 (6)	−0.0006 (6)
C14	0.0211 (9)	0.0290 (9)	0.0173 (7)	0.0001 (7)	−0.0033 (7)	−0.0060 (6)
C15	0.0285 (11)	0.0413 (12)	0.0426 (12)	0.0099 (9)	−0.0016 (9)	−0.0125 (9)
C16	0.0228 (10)	0.0382 (10)	0.0386 (11)	0.0087 (9)	−0.0051 (8)	−0.0071 (9)

Geometric parameters (Å, º)

Ni1—N21	2.0434 (15)	C5—H5A	0.9800
Ni1—N21^{i}	2.0434 (15)	C5—H5B	0.9800
Ni1—O2	2.0951 (11)	C5—H5C	0.9800
Ni1—O2^{i}	2.0951 (11)	C6—H6A	0.9800
Ni1—O1	2.0954 (11)	C6—H6B	0.9800
Ni1—O1^{i}	2.0954 (11)	C6—H6C	0.9800
N21—C21	1.160 (2)	N11—C14	1.338 (2)
C21—S21	1.6411 (18)	N11—C11	1.340 (2)
O1—H1O1	0.8399	N12—C12	1.335 (2)
O1—H2O1	0.8400	N12—C13	1.342 (2)
O2—H1O2	0.8399	C11—C12	1.396 (2)
O2—H2O2	0.8400	C11—C15	1.496 (3)
N1—C4	1.335 (3)	C12—H12	0.9500
N1—C1	1.341 (2)	C13—C14	1.389 (2)
N2—C2	1.338 (2)	C13—C16	1.500 (3)
N2—C3	1.339 (2)	C14—H14	0.9500
C1—C2	1.388 (2)	C15—H15A	0.9800
C1—C5	1.496 (3)	C15—H15B	0.9800
C2—H2	0.9500	C15—H15C	0.9800
C3—C4	1.390 (2)	C16—H16A	0.9800
C3—C6	1.497 (3)	C16—H16B	0.9800
C4—H4	0.9500	C16—H16C	0.9800
N21—Ni1—N21^{i}	180.0	C1—C5—H5B	109.5
N21—Ni1—O2	91.03 (5)	H5A—C5—H5B	109.5
N21^{i}—Ni1—O2	88.97 (5)	C1—C5—H5C	109.5
N21—Ni1—O2^{i}	88.97 (5)	H5A—C5—H5C	109.5
N21^{i}—Ni1—O2^{i}	91.03 (5)	H5B—C5—H5C	109.5
O2—Ni1—O2^{i}	180.00 (4)	C3—C6—H6A	109.5
N21—Ni1—O1	87.87 (5)	C3—C6—H6B	109.5
N21^{i}—Ni1—O1	92.13 (5)	H6A—C6—H6B	109.5
O2—Ni1—O1	89.01 (5)	C3—C6—H6C	109.5
O2^{i}—Ni1—O1	90.99 (5)	H6A—C6—H6C	109.5
N21—Ni1—O1^{i}	92.13 (5)	H6B—C6—H6C	109.5
N21^{i}—Ni1—O1^{i}	87.87 (5)	C14—N11—C11	117.34 (15)
O2—Ni1—O1^{i}	90.99 (5)	C12—N12—C13	117.16 (15)
O2^{i}—Ni1—O1^{i}	89.01 (5)	N11—C11—C12	119.63 (16)
O1—Ni1—O1^{i}	180.00 (5)	N11—C11—C15	118.88 (16)
C21—N21—Ni1	171.90 (14)	C12—C11—C15	121.48 (16)
N21—C21—S21	178.72 (15)	N12—C12—C11	123.00 (15)
Ni1—O1—H1O1	109.7	N12—C12—H12	118.5
Ni1—O1—H2O1	120.4	C11—C12—H12	118.5
H1O1—O1—H2O1	106.7	N12—C13—C14	119.93 (16)
Ni1—O2—H1O2	108.8	N12—C13—C16	118.09 (16)
Ni1—O2—H2O2	108.9	C14—C13—C16	121.97 (16)
H1O2—O2—H2O2	109.5	N11—C14—C13	122.91 (16)

C4—N1—C1	117.25 (15)	N11—C14—H14	118.5
C2—N2—C3	117.32 (15)	C13—C14—H14	118.5
N1—C1—C2	119.81 (16)	C11—C15—H15A	109.5
N1—C1—C5	117.87 (17)	C11—C15—H15B	109.5
C2—C1—C5	122.31 (17)	H15A—C15—H15B	109.5
N2—C2—C1	122.89 (16)	C11—C15—H15C	109.5
N2—C2—H2	118.6	H15A—C15—H15C	109.5
C1—C2—H2	118.6	H15B—C15—H15C	109.5
N2—C3—C4	119.71 (17)	C13—C16—H16A	109.5
N2—C3—C6	117.85 (17)	C13—C16—H16B	109.5
C4—C3—C6	122.44 (17)	H16A—C16—H16B	109.5
N1—C4—C3	122.99 (17)	C13—C16—H16C	109.5
N1—C4—H4	118.5	H16A—C16—H16C	109.5
C3—C4—H4	118.5	H16B—C16—H16C	109.5
C1—C5—H5A	109.5		

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*1···N12	0.84	1.99	2.8284 (18)	174
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Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*+1/2, *y*, −*z*+1/2; (iii) −*x*+1/2, *y*+1/2, *z*.