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Crystal structure of bis(dimethylammonium) hexaaquanickel(II) bis(sulfate) dihydrate

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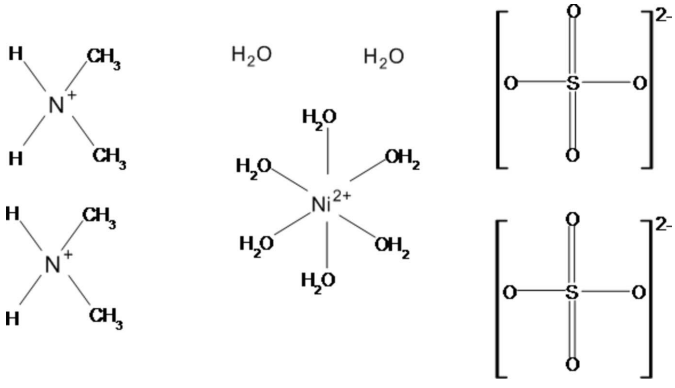
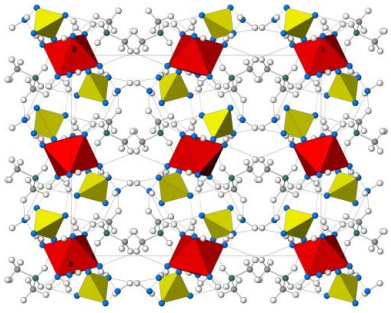
In the title salt, $(C_2H_8N)_2[Ni(H_2O)_6](SO_4)_2\cdot 2H_2O$, the Ni^{II} cation is located on a centre of inversion and exhibits a slightly distorted octahedral arrangement of water molecules. The Ni—O bond lengths in the complex $[Ni(H_2O)_6]^{2+}$ cation show a distribution as in the related Tutton salt $(NH_4)_2[Ni(H_2O)_6](SO_4)_2$, but are longer in average [2.056 (13) *versus* 2.037 (12) Å]. The noncoordinating water molecules and dimethylammonium cations connect the sulfate and $[Ni(H_2O)_6]^{2+}$ octahedra *via* O—H···O and N—H···O hydrogen bonds from weak up to medium strength into a three-dimensional framework whereby the complex metal cations and sulfate anions are arranged in sheets parallel (001).

1. Chemical context

In the course of a systematic search for new 'double salts' of simple secondary amines and divalent cations of various inorganic acids, the structure of $[(CH_3)_2NH_2][Cu(HSO_4)(SO_4)(H_2O)_4]$ has been described previously (Held, 2014). In continuation of these studies, copper(II) was replaced by nickel(II), yielding crystals of the title compound with composition $(C_2H_8N)_2[Ni(H_2O)_6](SO_4)_2\cdot 2H_2O$.





2. Structural commentary

The asymmetric unit of the title compound consists of one $[NH_2(CH_3)]^+$ cation, one Ni^{2+} cation situated on an inversion centre (Wyckoff position 4*a*), one SO_4^{2-} anion and four water molecules, one of which is not coordinating to the metal cation (Fig. 1). The Ni^{II} cation exhibits a slightly distorted octahedral arrangement of the water molecules. The Ni—O distances show the same bond lengths distribution [mean 2.055 (12) Å], as in the related Tutton salt $(NH_4)_2[Ni(H_2O)_6](SO_4)_2$ (Grimes *et al.*, 1963), but are slightly longer (Δd = 0.02 Å). The Ni^{II} cation reaches an overall bond valence sum (Brown & Altermatt, 1985) of 2.03 valence units. The S—O distances are nearly equal [mean 1.463 (8) Å], however, the O—S—O angles vary clearly [average bond angle 109.5 (8)°].

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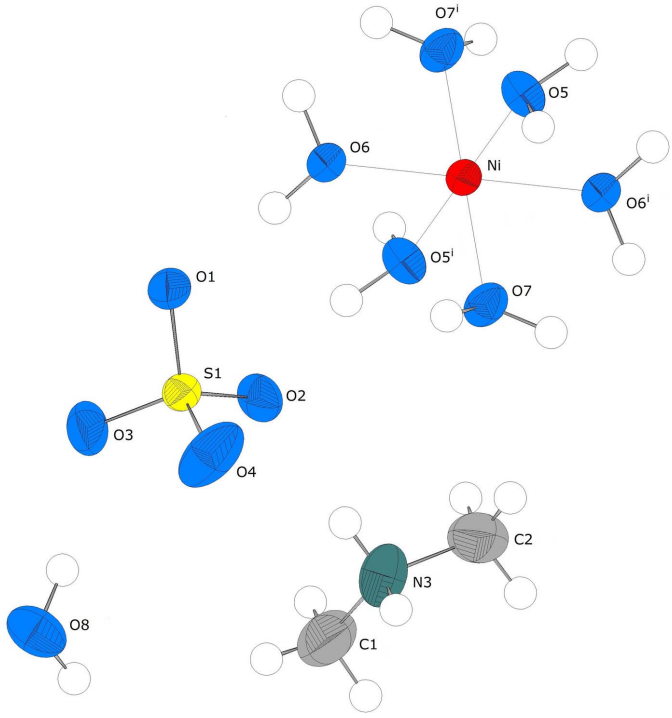

Figure 1
The molecular entities in the structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x, -y+1, -z-1$.]

3. Supramolecular features

Hydrogen bonds of weak up to medium strength involving coordinating and noncoordinating water molecules as donor groups and O atoms of the sulfate anions as acceptor groups interconnect neighbouring $[Ni(H_2O)_6]^{2+}$ octahedra. Together with relatively weaker N—H···O hydrogen bonds of the ammonium H atoms to sulfate anions, a three-dimensional framework is formed with pronounced formation of sheets of complex metal cations and sulfate anions parallel (001) (Table 1 and Fig. 2).

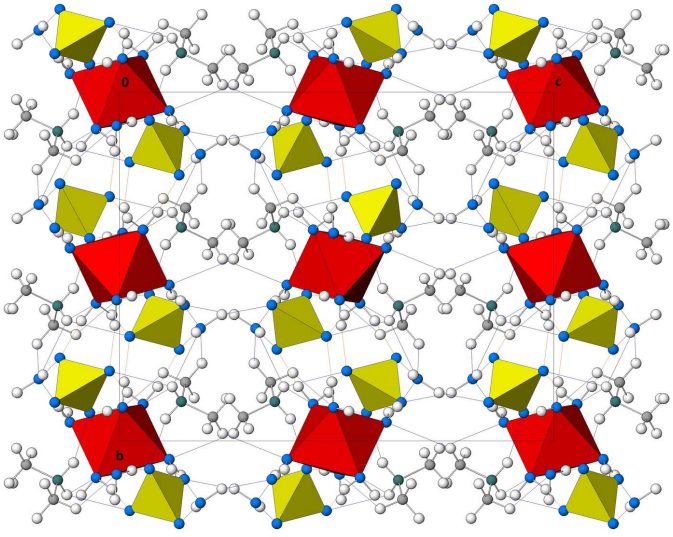

Figure 2
(100)-projection of the crystal structure of the title compound. Colour scheme: (SO_4) tetrahedra yellow, $[Ni(OH_2)_6]$ octahedra red, O blue, N green, C grey and H colourless. H···O bonds up to 1.8 Å are given as orange dashed lines and from 1.85 to 2.7 Å as light-blue dashed lines.

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H51···O2^{i}	0.97 (1)	1.77 (2)	2.727 (5)	166 (5)
O5—H52···O8	0.98 (1)	1.84 (1)	2.814 (6)	176 (7)
O6—H61···O3^{ii}	0.97 (1)	1.73 (2)	2.689 (5)	169 (6)
O6—H62···O1	0.98 (1)	1.78 (2)	2.731 (5)	164 (5)
O7—H71···O4^{iii}	0.97 (1)	1.78 (2)	2.730 (6)	164 (5)
O7—H72···O1^{iv}	0.98 (1)	1.78 (2)	2.745 (5)	173 (7)
O8—H81···O3^{iii}	0.98 (1)	2.01 (2)	2.962 (6)	166 (6)
O8—H82···O2^{v}	0.98 (1)	1.93 (3)	2.856 (6)	158 (7)
N3—H3B···O4^{vi}	0.90	2.02	2.835 (7)	151
N3—H3A···O6^{iv}	0.90	2.65	3.274 (6)	127

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

4. Synthesis and crystallization

The title compound was obtained by reaction of an aqueous solution of nickel(II) sulfate with dimethylamine and sulfuric acid (18 mol l^{-1}) in a stoichiometric ratio of 1:2:1. The resulting solution was kept at room temperature by cooling.

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_2H_8N)_2[Ni(H_2O)_6](SO_4)_2{\cdot}2H_2O$
M_r	487.13
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	295
a, b, c (Å)	8.9363 (6), 13.2370 (8), 16.4810 (14)
V (Å^3)	1949.5 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.28
Crystal size (mm)	0.29 × 0.27 × 0.26
Data collection	
Diffractometer	Enraf–Nonius MACH3
Absorption correction	ψ scan (North *et al.*, 1968)
T_{min}, T_{max}	0.935, 0.999
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4902, 1719, 962
R_{int}	0.107
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.123, 1.07
No. of reflections	1719
No. of parameters	148
No. of restraints	8
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.44, −0.41

Computer programs: *CAD-4 Software* (Enraf–Nonius, 1998), *MolEN* (Fair, 1990), *SIR97* (Altomare *et al.*, 1999), *ATOMS* (Dowty, 2011), *SHELXL97* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

The title compound crystallized by slow evaporation of the solvent at room temperature in form of light-green crystals with dimensions up to 4 mm within 12 weeks.

5. Refinement

Details of structure refinement are given in Table 2. All H atoms were clearly discernible from difference Fourier maps. However, riding-model contraints were applied to all H atoms in the least-squares refinement, with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms, and N—H = 0.90 Å and U_{iso}(H) = 1.2U_{eq}(N) for ammonium H atoms. The H atoms of water molecules were refined with a distance restraint of O—H = 0.98 Å and individual U_{iso} values for each H atom.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Dowty, E. (2011). *ATOMS*. Shape Software, Hidden Valley Road, Kingsport, Tennessee, USA.

Enraf–Nonius (1998). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.

Grimes, N. W., Kay, H. F. & Webb, M. W. (1963). *Acta Cryst.* **16**, 823–829.

Held, P. (2014). *Acta Cryst.* E**70**, m119.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

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Acta Cryst. (2014). E**70**, 403-405 [doi:10.1107/S160053681402234X]

Crystal structure of bis(dimethylammonium) hexaaquanickel(II) bis(sulfate) dihydrate

Peter Held

Computing details

Data collection: *CAD-4 Software* (Enraf–Nonius, 1998); cell refinement: *CAD-4 Software* (Enraf–Nonius, 1998); data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 2011); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and puplCIF (Westrip, 2010).

Bis(dimethylammonium) hexaaquanickel(II) bis(sulfate) dihydrate

Crystal data

$(C_2H_8N)_2[Ni(H_2O)_6](SO_4)_2{\cdot}2H_2O$
M_r = 487.13
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
a = 8.9363 (6) Å
b = 13.2370 (8) Å
c = 16.4810 (14) Å
V = 1949.5 (2) Å^3
Z = 4
F(000) = 1032
D_x = 1.660 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 5.5–10.1°
μ = 1.28 mm^{-1}
T = 295 K
Prism, light green
0.29 × 0.27 × 0.26 mm

Data collection

Enraf–Nonius MACH3 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
/w2/q scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.935, T_{max} = 0.999
4902 measured reflections
1719 independent reflections
962 reflections with $I > 2\sigma(I)$
R_{int} = 0.107
θ_{max} = 25.0°, θ_{min} = 2.5°
h = −10→10
k = −15→15
l = −19→19
3 standard reflections every 100 reflections
intensity decay: 0.3%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.123
S = 1.07
1719 reflections
148 parameters
8 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

$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 0.0324P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0267 (19)

Special details

Experimental. A suitable single-crystal was carefully selected under a polarizing microscope and mounted in a glass capillary.

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.

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 $F^2 > \sigma(F^2)$ 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}
Ni	0.0000	0.5000	−0.5000	0.0269 (3)
S1	0.44455 (15)	0.65768 (10)	−0.40485 (8)	0.0314 (4)
O1	0.3690 (4)	0.7003 (3)	−0.4766 (2)	0.0446 (11)
O2	0.3354 (4)	0.6104 (3)	−0.3508 (2)	0.0424 (11)
O3	0.5247 (5)	0.7376 (3)	−0.3626 (3)	0.0617 (13)
O4	0.5509 (6)	0.5805 (3)	−0.4313 (3)	0.0764 (16)
O5	−0.0494 (5)	0.4469 (3)	−0.6145 (2)	0.0382 (10)
H51	−0.150 (3)	0.420 (4)	−0.619 (3)	0.06 (2)*
H52	0.023 (7)	0.401 (5)	−0.639 (5)	0.12 (3)*
O6	0.1383 (4)	0.6054 (3)	−0.5541 (2)	0.0339 (9)
H61	0.090 (6)	0.656 (3)	−0.588 (3)	0.07 (2)*
H62	0.209 (5)	0.639 (4)	−0.518 (3)	0.07 (2)*
O7	0.1783 (4)	0.4042 (3)	−0.4930 (2)	0.0379 (9)
H71	0.264 (4)	0.415 (5)	−0.528 (3)	0.07 (2)*
H72	0.169 (9)	0.3310 (10)	−0.490 (4)	0.11 (3)*
O8	0.1689 (5)	0.3224 (4)	−0.6862 (2)	0.0535 (12)
H81	0.275 (2)	0.311 (5)	−0.676 (4)	0.10 (3)*
H82	0.177 (10)	0.361 (5)	−0.736 (3)	0.12 (3)*
N3	0.0336 (6)	0.1126 (4)	−0.6424 (3)	0.0537 (15)
H3A	0.1022	0.1550	−0.6213	0.064*
H3B	0.0189	0.0628	−0.6061	0.064*
C1	0.0946 (11)	0.0689 (5)	−0.7152 (5)	0.097 (3)
H1A	0.1864	0.0346	−0.7027	0.145*
H1B	0.1138	0.1214	−0.7541	0.145*
H1C	0.0243	0.0216	−0.7375	0.145*
C2	−0.1071 (8)	0.1681 (6)	−0.6520 (5)	0.071 (2)
H2A	−0.1374	0.1951	−0.6005	0.106*
H2B	−0.1830	0.1231	−0.6720	0.106*
H2C	−0.0930	0.2223	−0.6899	0.106*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni	0.0289 (5)	0.0233 (5)	0.0284 (5)	0.0004 (5)	−0.0020 (4)	0.0003 (5)
S1	0.0293 (7)	0.0309 (7)	0.0340 (8)	−0.0008 (6)	−0.0010 (6)	0.0055 (6)
O1	0.055 (3)	0.040 (2)	0.038 (2)	−0.009 (2)	−0.0177 (19)	0.0099 (18)
O2	0.031 (2)	0.053 (3)	0.043 (2)	−0.0083 (19)	0.0059 (19)	0.007 (2)
O3	0.083 (3)	0.054 (3)	0.047 (3)	−0.033 (3)	−0.027 (2)	0.015 (2)
O4	0.066 (3)	0.059 (3)	0.104 (4)	0.026 (3)	0.040 (3)	0.029 (3)
O5	0.032 (2)	0.045 (2)	0.038 (2)	−0.005 (2)	−0.0017 (19)	−0.0058 (19)
O6	0.036 (2)	0.029 (2)	0.037 (2)	−0.0031 (18)	−0.0059 (18)	0.0067 (18)
O7	0.032 (2)	0.032 (2)	0.050 (3)	0.0070 (18)	0.008 (2)	0.007 (2)
O8	0.041 (3)	0.080 (3)	0.040 (3)	−0.003 (3)	0.000 (2)	−0.008 (3)
N3	0.069 (4)	0.041 (3)	0.051 (3)	0.004 (3)	−0.016 (3)	−0.005 (3)
C1	0.147 (9)	0.049 (5)	0.094 (7)	0.008 (5)	0.065 (6)	0.013 (4)
C2	0.051 (4)	0.078 (6)	0.082 (5)	−0.001 (4)	0.011 (4)	0.021 (5)

Geometric parameters (Å, º)

Ni—O7^{i}	2.040 (3)	O7—H71	0.974 (10)
Ni—O7	2.040 (3)	O7—H72	0.975 (10)
Ni—O5	2.061 (4)	O8—H81	0.975 (10)
Ni—O5^{i}	2.061 (4)	O8—H82	0.976 (10)
Ni—O6	2.066 (4)	N3—C1	1.440 (8)
Ni—O6^{i}	2.066 (4)	N3—C2	1.464 (8)
S1—O3	1.455 (4)	N3—H3A	0.9000
S1—O4	1.461 (4)	N3—H3B	0.9000
S1—O2	1.461 (4)	C1—H1A	0.9600
S1—O1	1.474 (4)	C1—H1B	0.9600
O5—H51	0.974 (10)	C1—H1C	0.9600
O5—H52	0.976 (10)	C2—H2A	0.9600
O6—H61	0.973 (10)	C2—H2B	0.9600
O6—H62	0.976 (10)	C2—H2C	0.9600
O7^{i}—Ni—O7	180.0 (2)	Ni—O6—H62	116 (4)
O7^{i}—Ni—O5	89.60 (16)	H61—O6—H62	109 (5)
O7—Ni—O5	90.40 (16)	Ni—O7—H71	119 (4)
O7^{i}—Ni—O5^{i}	90.40 (16)	Ni—O7—H72	123 (5)
O7—Ni—O5^{i}	89.60 (16)	H71—O7—H72	104 (6)
O5—Ni—O5^{i}	180.0	H81—O8—H82	99 (6)
O7^{i}—Ni—O6	91.33 (15)	C1—N3—C2	115.8 (6)
O7—Ni—O6	88.67 (15)	C1—N3—H3A	108.3
O5—Ni—O6	87.90 (15)	C2—N3—H3A	108.3
O5^{i}—Ni—O6	92.10 (15)	C1—N3—H3B	108.3
O7^{i}—Ni—O6^{i}	88.67 (15)	C2—N3—H3B	108.3
O7—Ni—O6^{i}	91.33 (15)	H3A—N3—H3B	107.4
O5—Ni—O6^{i}	92.10 (15)	N3—C1—H1A	109.5
O5^{i}—Ni—O6^{i}	87.90 (15)	N3—C1—H1B	109.5

O6—Ni—O6^{i}	180.00 (19)	H1A—C1—H1B	109.5
O3—S1—O4	109.3 (3)	N3—C1—H1C	109.5
O3—S1—O2	110.4 (3)	H1A—C1—H1C	109.5
O4—S1—O2	108.4 (3)	H1B—C1—H1C	109.5
O3—S1—O1	109.3 (2)	N3—C2—H2A	109.5
O4—S1—O1	109.0 (3)	N3—C2—H2B	109.5
O2—S1—O1	110.3 (2)	H2A—C2—H2B	109.5
Ni—O5—H51	113 (3)	N3—C2—H2C	109.5
Ni—O5—H52	117 (5)	H2A—C2—H2C	109.5
H51—O5—H52	110 (6)	H2B—C2—H2C	109.5
Ni—O6—H61	117 (4)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H51···O2^{i}	0.97 (1)	1.77 (2)	2.727 (5)	166 (5)
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N3—H3*A*···O6^{iv}	0.90	2.65	3.274 (6)	127

Symmetry codes: (i) −*x*, −*y*+1, −*z*−1; (ii) *x*−1/2, −*y*+3/2, −*z*−1; (iii) −*x*+1, −*y*+1, −*z*−1; (iv) −*x*+1/2, *y*−1/2, *z*; (v) −*x*+1/2, −*y*+1, *z*−1/2; (vi) *x*−1/2, −*y*+1/2, −*z*−1.