

trans-Diaquabis(1*H*-imidazole-4-carboxylato- κ^2 N³,O⁴)nickel(II)

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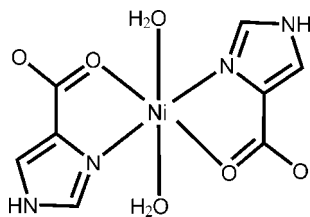
Received 24 April 2011; accepted 17 May 2011

Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.027; wR factor = 0.070; data-to-parameter ratio = 11.9.

In the title complex, $[\text{Ni}(\text{C}_4\text{H}_3\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2]$, the Ni^{II} ion is located on an inversion center and shows a distorted octahedral geometry, defined by two *N,O*-bidentate 1*H*-imidazole-4-carboxylate ligands in the equatorial plane and two water molecules in the axial positions. Intermolecular N—H···O hydrogen bonds link the complex molecules into layers parallel to (10 $\bar{2}$), which are further linked into a three-dimensional supramolecular network through O—H···O hydrogen bonds.

Related literature

For general background to the design and synthesis of coordination polymers, see: Choi & Jeon (2003); Moulton & Zaworotko (2001); Roesky & Andruh (2003); Tao *et al.* (2000). For complexes with imidazole-4,5-dicarboxylic acid, see: Alkordi *et al.* (2009); Lu *et al.* (2009); Sun *et al.* (2005). For related structures, see: Gryz *et al.* (2007); Haggag (2005); Starosta & Leciejewicz (2006); Xu *et al.* (2008); Yin *et al.* (2009); Zheng *et al.* (2011).



Experimental

Crystal data

$[\text{Ni}(\text{C}_4\text{H}_3\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2]$

$M_r = 316.91$

Monoclinic, $P2_1/c$

$a = 6.6123$ (18) Å

$b = 12.267$ (3) Å

$c = 7.239$ (2) Å

$\beta = 101.059$ (3)°

$V = 576.2$ (3) Å³

$Z = 2$

Mo $K\alpha$ radiation

$\mu = 1.72$ mm⁻¹

$T = 298$ K

$0.48 \times 0.36 \times 0.32$ mm

Data collection

Bruker APEXII CCD
diffractometer

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.493$, $T_{\max} = 0.610$

2878 measured reflections

1043 independent reflections

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

$R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.070$

$S = 1.07$

1043 reflections

88 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.25$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.42$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H2N···O2 ⁱ	0.86	2.16	2.942 (3)	152
N2—H2N···O1 ⁱ	0.86	2.36	3.130 (2)	149
O1W—H1WA···O2 ⁱⁱ	0.83	1.94	2.762 (2)	169
O1W—H1WB···O2 ⁱⁱⁱ	0.84	1.94	2.7654 (19)	168

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

This work was supported financially by the National Natural Science Foundation of China (grant No. 21003053) and the Natural Science Foundation of Guangdong (grant No. 10451063101004667).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2425).

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supporting information

Acta Cryst. (2011). E67, m865 [doi:10.1107/S1600536811018824]

trans*-Diaquabis(1*H*-imidazole-4-carboxylato- κ^2N^3,O^4)nickel(II)*Shengrun Zheng, Songliang Cai, Jun Fan and Weiguang Zhang****S1. Comment**

The rational design and synthesis of coordination polymers have received extensive attention over the past decades (Moulton & Zaworotko, 2001; Roesky & Andruh, 2003). The choice of suitable ligands is an important factor that greatly affects the structure and stabilization of the coordination architecture (Choi & Jeon, 2003; Tao *et al.*, 2000). Recently, our group has focused on constructing coordination polymers based on *N*-heterocyclic carboxylic acids (Zheng *et al.*, 2011). 1*H*-Imidazole-4-carboxylic acid (H₂imc), which is recognized as efficient N/O donors exhibiting versatile coordination behaviors and potential hydrogen-bonding abilities, remains largely unexplored, compared with its analogue imidazole-4,5-dicarboxylic acid (Alkordi *et al.*, 2009; Lu *et al.*, 2009; Sun *et al.*, 2005). A few of mononuclear complexes based on the H₂imc ligand have been reported (Gryz *et al.*, 2007; Haggag, 2005; Starosta & Leciejewicz, 2006; Yin *et al.*, 2009). In this work, we report the synthesis and structure of a new Ni^{II} complex, which was obtained by the solvothermal reaction of Ni(ClO₄)₂·6H₂O and H₂imc.

The asymmetric unit contains a half of [Ni(Himc)₂(H₂O)₂] formula unit, with the Ni^{II} ion lying on an inversion center. The Ni^{II} ion exhibits a distorted octahedral geometry, in which two bidentate chelating Himc ligands are located in the equatorial plane, forming two stable five-membered rings with metal ion, and the axial sites are occupied by two coordinated water molecules (Fig. 1). The Ni—O distances range from 2.0764 (13) to 2.0947 (17) Å and Ni—N bonds have the value of 2.0502 (17) Å, which are similar to the reported Ni^{II} complexes with imidazole-based carboxylate ligands (Xu *et al.*, 2008).

In the crystal, each complex molecule is joined to four adjacent ones *via* N2—H2···O1ⁱⁱ and N2—H2···O2ⁱⁱ hydrogen bonds between the imidazole N—H group and carboxylate O atoms (Table 1) [symmetry code: (ii) $x + 1, -y + 1/2, z + 1/2$], generating a two-dimensional hydrogen-bonded sheet parallel to (1 0 $\bar{2}$) (Fig. 2). These sheets are further linked by O—H···O hydrogen bonds involving the coordinated water molecules (O1W) and carboxylate O atoms (O2), resulting in a three-dimensional supramolecular network (Fig. 3).

S2. Experimental

A mixture of Ni(ClO₄)₂·6H₂O (41.9 mg, 0.10 mmol), H₂imc (11.2 mg, 0.10 mmol), NaOH (4.0 mg, 0.10 mmol) and EtOH/H₂O (*v/v* 1:1, 6 ml) was sealed in a 10 ml Teflon-lined stainless-steel reactor, which was heated to 100°C for 48 h under autogenous pressure, and then slowly cooled to room temperature at a rate of 5°C h⁻¹. Pale green block crystals of the title compound were isolated, washed with distilled water and dried in air (yield: 78%). IR (KBr, cm⁻¹): 3340 s, 2923 m, 2853 w, 2350 w, 1598 s, 1461 m, 1427 w, 1402 w, 1357 m, 1287 w, 1260 w, 1091 s, 1039 m, 854 w, 806 w, 723 m, 655 w, 544 m, 456w.

S3. Refinement

C- and N-bound H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 and N—H = 0.86 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. H atoms of water molecule were located from a difference Fourier map and refined as riding atoms with O—H = 0.84 Å.

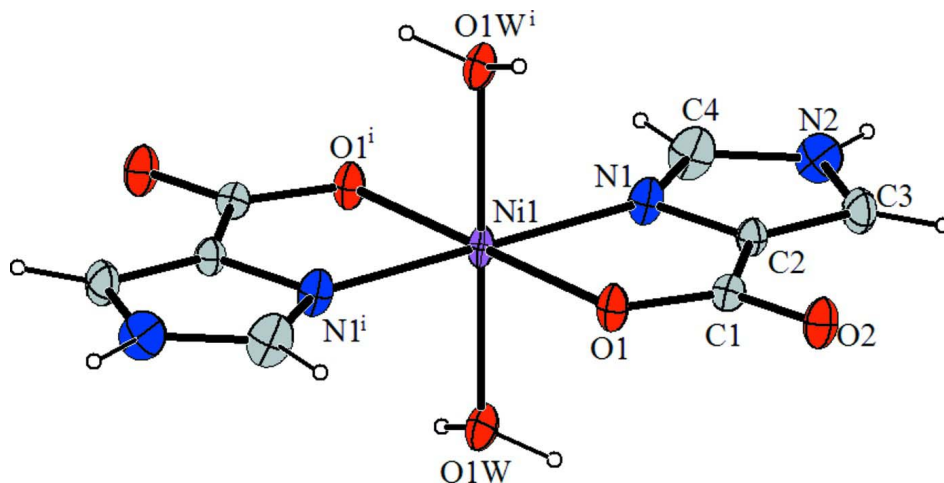


Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level.

[Symmetry code: (i) $1 - x, -y, -z$.]

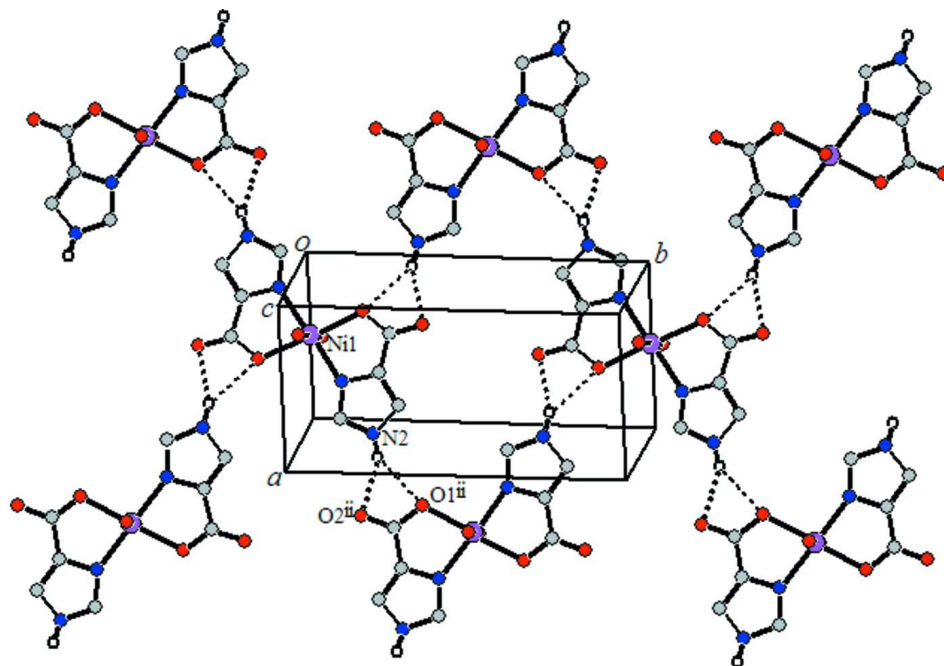


Figure 2

The crystal packing of the title compound, showing the two-dimensional hydrogen-bonded network. Hydrogen bonds are shown as dashed lines.

[Symmetry code: (ii) $x + 1, -y + 1/2, z + 1/2$.]

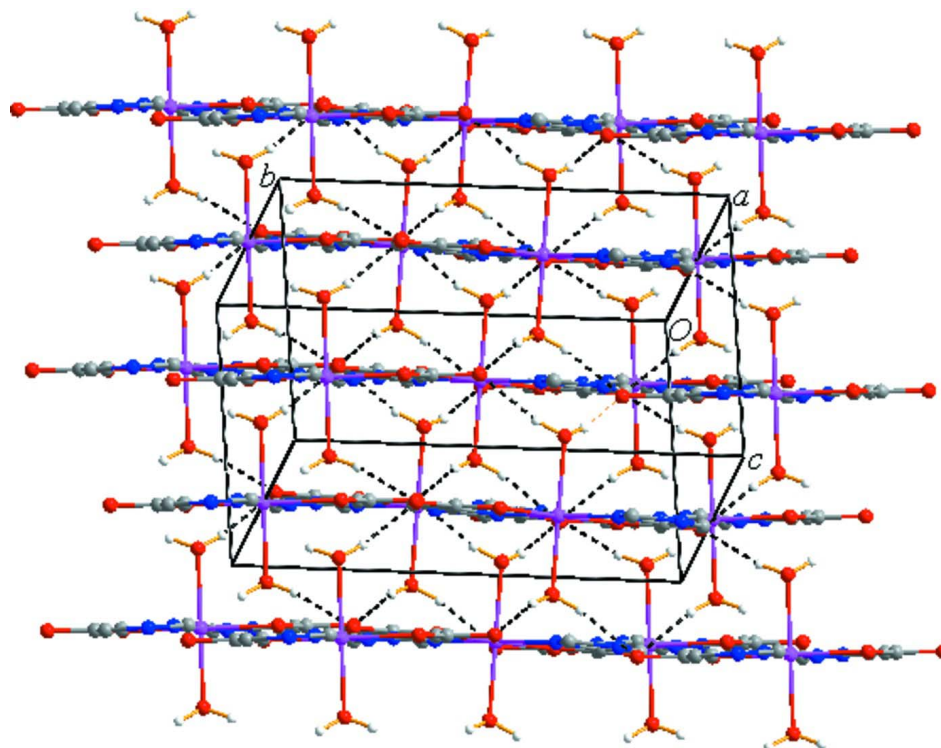


Figure 3

The crystal packing of the title compound, showing the three-dimensional hydrogen-bonded network. Hydrogen bonds are shown as dashed lines.

***trans*-Diaquabis(1*H*-imidazole-4-carboxylato- κ^2N^3,O^4)nickel(II)**

Crystal data

[Ni(C₄H₃N₂O₂)₂(H₂O)₂]

$M_r = 316.91$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 6.6123$ (18) Å

$b = 12.267$ (3) Å

$c = 7.239$ (2) Å

$\beta = 101.059$ (3)°

$V = 576.2$ (3) Å³

$Z = 2$

$F(000) = 324$

$D_x = 1.826$ Mg m⁻³

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

Cell parameters from 1803 reflections

$\theta = 3.1$ – 27.8 °

$\mu = 1.72$ mm⁻¹

$T = 298$ K

Block, pale green

$0.48 \times 0.36 \times 0.32$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.493$, $T_{\max} = 0.610$

2878 measured reflections

1043 independent reflections

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

$R_{\text{int}} = 0.027$

$\theta_{\max} = 25.2$ °, $\theta_{\min} = 3.1$ °

$h = -7 \rightarrow 7$

$k = -14 \rightarrow 14$

$l = -8 \rightarrow 7$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.070$

$S = 1.07$

1043 reflections

88 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

$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 0.1301P]$

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

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

$\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.5000	0.0000	0.0000	0.02288 (16)
N1	0.7437 (3)	0.09727 (13)	0.1157 (2)	0.0289 (4)
C3	0.8498 (3)	0.26678 (17)	0.1929 (3)	0.0331 (5)
H2	0.8537	0.3422	0.2070	0.040*
C4	0.9370 (3)	0.09539 (18)	0.2052 (3)	0.0401 (6)
H4	1.0157	0.0325	0.2312	0.048*
C2	0.6866 (3)	0.20552 (15)	0.1070 (3)	0.0226 (4)
N2	1.0046 (3)	0.19580 (17)	0.2536 (3)	0.0411 (5)
H2N	1.1260	0.2125	0.3132	0.049*
O2	0.4160 (2)	0.32925 (10)	-0.0090 (2)	0.0322 (4)
O1	0.3604 (2)	0.15166 (10)	-0.0480 (2)	0.0270 (3)
O1W	0.4100 (3)	-0.00996 (9)	0.2616 (2)	0.0307 (4)
C1	0.4750 (3)	0.23191 (17)	0.0111 (2)	0.0225 (4)
H1WA	0.4644	-0.0632	0.3236	0.027*
H1WB	0.4254	0.0483	0.3241	0.027*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0221 (3)	0.0146 (2)	0.0284 (2)	0.00075 (12)	-0.00422 (15)	-0.00212 (12)
N1	0.0249 (10)	0.0224 (9)	0.0348 (9)	0.0037 (7)	-0.0057 (7)	-0.0029 (7)
C3	0.0268 (11)	0.0294 (11)	0.0410 (12)	-0.0075 (9)	0.0013 (9)	-0.0092 (9)
C4	0.0267 (13)	0.0401 (13)	0.0473 (13)	0.0096 (10)	-0.0089 (10)	-0.0050 (10)
C2	0.0213 (10)	0.0200 (9)	0.0249 (9)	-0.0018 (7)	-0.0001 (8)	-0.0020 (7)
N2	0.0179 (9)	0.0548 (12)	0.0455 (11)	-0.0031 (8)	-0.0066 (8)	-0.0147 (9)
O2	0.0348 (9)	0.0188 (7)	0.0385 (9)	0.0048 (6)	-0.0037 (6)	0.0020 (5)
O1	0.0211 (7)	0.0199 (7)	0.0348 (7)	0.0010 (6)	-0.0076 (6)	-0.0025 (6)
O1W	0.0403 (10)	0.0188 (7)	0.0306 (8)	0.0027 (6)	0.0008 (7)	-0.0008 (5)
C1	0.0243 (11)	0.0214 (11)	0.0204 (9)	0.0008 (7)	0.0008 (8)	0.0003 (7)

Geometric parameters (\AA , $^\circ$)

Ni1—N1	2.0502 (17)	C4—N2	1.334 (3)
Ni1—O1	2.0764 (13)	C4—H4	0.9300

Ni1—O1W	2.0947 (17)	C2—C1	1.473 (3)
N1—C4	1.318 (3)	N2—H2N	0.8600
N1—C2	1.379 (3)	O2—C1	1.256 (2)
C3—N2	1.352 (3)	O1—C1	1.266 (2)
C3—C2	1.363 (3)	O1W—H1WA	0.83
C3—H2	0.9300	O1W—H1WB	0.84
N1 ⁱ —Ni1—N1	180.00 (10)	N2—C3—H2	127.0
N1 ⁱ —Ni1—O1 ⁱ	80.58 (6)	C2—C3—H2	127.0
N1—Ni1—O1 ⁱ	99.42 (6)	N1—C4—N2	110.96 (19)
N1 ⁱ —Ni1—O1	99.42 (6)	N1—C4—H4	124.5
N1—Ni1—O1	80.58 (6)	N2—C4—H4	124.5
O1 ⁱ —Ni1—O1	180.00 (8)	C3—C2—N1	108.92 (18)
N1 ⁱ —Ni1—O1W ⁱ	90.11 (7)	C3—C2—C1	133.68 (19)
N1—Ni1—O1W ⁱ	89.89 (7)	N1—C2—C1	117.39 (16)
O1 ⁱ —Ni1—O1W ⁱ	90.53 (5)	C4—N2—C3	108.32 (18)
O1—Ni1—O1W ⁱ	89.47 (5)	C4—N2—H2N	125.8
N1 ⁱ —Ni1—O1W	89.89 (7)	C3—N2—H2N	125.8
N1—Ni1—O1W	90.11 (7)	C1—O1—Ni1	114.94 (12)
O1 ⁱ —Ni1—O1W	89.47 (5)	Ni1—O1W—H1WA	111.4
O1—Ni1—O1W	90.53 (5)	Ni1—O1W—H1WB	114.2
O1W ⁱ —Ni1—O1W	180.00 (11)	H1WA—O1W—H1WB	112.4
C4—N1—C2	105.70 (17)	O2—C1—O1	123.19 (17)
C4—N1—Ni1	143.40 (15)	O2—C1—C2	120.62 (18)
C2—N1—Ni1	110.80 (13)	O1—C1—C2	116.20 (17)
N2—C3—C2	106.10 (18)		
O1 ⁱ —Ni1—N1—C4	-2.4 (3)	C4—N1—C2—C1	179.45 (17)
O1—Ni1—N1—C4	177.6 (3)	Ni1—N1—C2—C1	-3.3 (2)
O1W ⁱ —Ni1—N1—C4	-92.9 (3)	N1—C4—N2—C3	-0.2 (3)
O1W—Ni1—N1—C4	87.1 (3)	C2—C3—N2—C4	0.2 (2)
O1 ⁱ —Ni1—N1—C2	-177.92 (12)	N1 ⁱ —Ni1—O1—C1	179.42 (13)
O1—Ni1—N1—C2	2.08 (12)	N1—Ni1—O1—C1	-0.58 (13)
O1W ⁱ —Ni1—N1—C2	91.56 (13)	O1W ⁱ —Ni1—O1—C1	-90.55 (13)
O1W—Ni1—N1—C2	-88.44 (13)	O1W—Ni1—O1—C1	89.45 (13)
C2—N1—C4—N2	0.2 (2)	Ni1—O1—C1—O2	178.85 (13)
Ni1—N1—C4—N2	-175.53 (18)	Ni1—O1—C1—C2	-1.03 (19)
N2—C3—C2—N1	-0.1 (2)	C3—C2—C1—O2	2.5 (3)
N2—C3—C2—C1	-179.5 (2)	N1—C2—C1—O2	-176.88 (16)
C4—N1—C2—C3	0.0 (2)	C3—C2—C1—O1	-177.7 (2)
Ni1—N1—C2—C3	177.21 (13)	N1—C2—C1—O1	3.0 (2)

Symmetry code: (i) $-x+1, -y, -z$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2N \cdots O2 ⁱⁱ	0.86	2.16	2.942 (3)	152

N2—H2N···O1 ⁱⁱ	0.86	2.36	3.130 (2)	149
O1W—H1WA···O2 ⁱⁱⁱ	0.83	1.94	2.762 (2)	169
O1W—H1WB···O2 ^{iv}	0.84	1.94	2.7654 (19)	168

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