Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Tetraaqua(2,2′-bipyridine-5,5′-dicarboxylato-κ^2N,N')nickel(II) dihydrate

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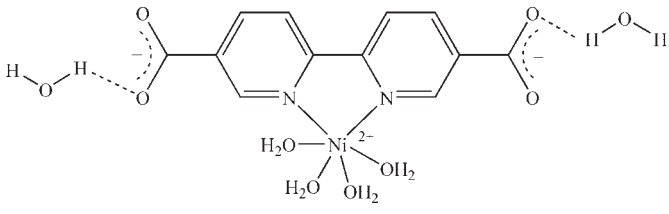
Received 2 September 2009; accepted 5 September 2009

Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.002 Å; R factor = 0.025; wR factor = 0.065; data-to-parameter ratio = 12.3.

In the title compound, $[Ni(C_{12}H_6N_2O_4)(H_2O)_4]\cdot 2H_2O$, obtained from a basic solution of 2,2′-bipyridine-5,5′-dicarboxylate and nickel(II) chloride in water, the central Ni(II) cation (site symmetry 2) is coordinated by two N atoms from the 2,2′-bipyridine-5,5′-dicarboxylate ligand and four aqua O atoms. The N—Ni—N angle is 78.64 (8)°. Weak but significant π–π stacking interactions exist between the pyridine rings with a centroid–centroid distance of 3.652 (8) Å. In addition, four O atoms of the two carboxyl groups form hydrogen bonds with both coordinated and uncoordinated water molecules, forming an infinite three-dimensional network.

Related literature

For attempts to synthesize 5,5′- and 6,6′-substituted 2,2′-bipyridine derivatives, see: He *et al.* (2009); Karaca *et al.* (2009); Yousefi *et al.* (2008).



Experimental

Crystal data

$[Ni(C_{12}H_6N_2O_4)(H_2O)_4]\cdot 2H_2O$
M_r = 408.97
Monoclinic, $C2/c$
a = 12.4787 (2) Å
b = 9.8152 (2) Å
c = 12.6533 (2) Å
β = 92.107 (2)°
V = 1548.74 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.31 mm^{-1}
T = 120 K
0.18 × 0.16 × 0.10 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.730, T_{max} = 0.828
8276 measured reflections
1691 independent reflections
1379 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.065
S = 0.98
1691 reflections
138 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H52···O3^{i}	0.837 (10)	2.178 (16)	2.9566 (19)	155 (3)
O2—H22···O3^{ii}	0.834 (10)	1.921 (12)	2.7410 (18)	168 (3)
O5—H51···O4^{iii}	0.834 (10)	1.913 (11)	2.7286 (19)	166 (2)
O2—H21···O4^{iv}	0.833 (10)	1.852 (10)	2.6831 (17)	175 (2)
O1—H11···O4^{iv}	0.843 (9)	2.650 (17)	3.1740 (18)	121.6 (16)
O1—H11···O3^{iv}	0.843 (9)	2.097 (10)	2.9386 (18)	175.9 (19)
O1—H12···O5	0.834 (10)	1.861 (11)	2.688 (2)	171 (3)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The author thanks the financial support of Natural Foundation of Heilongjiang Province.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2636).

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supplementary materials

Acta Cryst. (2009). E**65**, m1207 [**doi:10.1107/S1600536809035910**]

Tetraaqua(2,2'-bipyridine-5,5'-dicarboxylato-κ^2N,N')nickel(II) dihydrate

H. Yang

Comment

2,2'-Bipyridine was used very commonly as ending complexing ligand. Great efforts have been made to synthesize 5,5' and 6,6' position substituted derivatives (He *et al.*, 2009; Karaca *et al.*, 2009; Yousefi *et al.*, 2008). Here we reported the crystal structure of a complexing compound of Ni(II) coordinating to 4,4'dicarboxyl substituted 2,2'-bipyridine derivative.

The central Ni cation coordinated to two N atoms from dianions of one 2,2'-bipyridine-5,5'-dicarboxylate and four O atoms from four waters, forming a distorted octahedral system. Ni(II) cation lies on the twofold axis of the crystal lattice. Two Ni—N bonds were generated by *C*2 symmetry operation from each other with bond length 2.0706 (14). Four Ni—O bond lengths are nearly equal, two of which 2.0610 (12), and another two 2.0801 (13). Each of two equivalent carboxyl anions has two unequivalent oxygen atoms, C—O bond lengths of which are equalized to be 1.266 (2) and 1.254 (2), respectively. All O atoms of carboxyls formed hydrogen bonds with both complexed waters from another complexing supermolecule and free waters into three dimentional infinite hydrgon bonding network, which stablized the whole crystal structure, along with pi-pi stacking of aromatic pyridine rings.

Experimental

A solution of 2,2'-bipyridine-5,5'-dicarboxylate (23.2 mg, 0.1 mmol) and $NiCl_2·6H_2O$ (23.8 mg, 0.1 mmol) was added an aqueous solution of NaOH (0.1 mmol/ml) to adjust pH as 7.0–7.5 at room temperature. A small amount of white precipitate was removed from the resulting solution. Prism colorless crystals were obtained by slow evaporation at room temperature over a period of 10 days.

Refinement

All H atoms bonded to O atoms of ligand water and free water molecules were located in a difference map, and the distances of the O–H bonds were fixed to 0.82 Å. The other H atoms were placed in calculated positions and refined as riding, with C–H = 0.93 Å, and U_{iso}(H) = 1.2 U_{eq}(C).

Figures

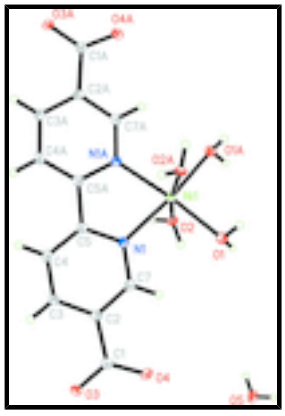

Fig. 1. The molecular structure with atom labels and 30% probability displacement ellipsoids for non-H atoms.

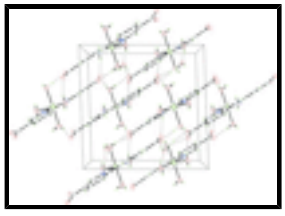

Fig. 2. The packing diagram of molecules, viewed down the *b* axis, with the weak interactions shown as dashed lines.

Tetraaqua(2,2'-bipyridine-5,5'-dicarboxylato-κ^2N,N') nickel(II) dihydrate

Crystal data

$[Ni(C_{12}H_6N_2O_4)(H_2O)_4]\cdot 2H_2O$	F_{000} = 848.0
M_r = 408.97	D_x = 1.754 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 8276 reflections
a = 12.4787 (2) Å	θ = 3.1–27.0º
b = 9.8152 (2) Å	μ = 1.31 mm^{-1}
c = 12.6533 (2) Å	*T* = 120 K
β = 92.107 (2)º	Prism, colourless
V = 1548.74 (5) Å^3	0.18 × 0.16 × 0.10 mm
Z = 4	

Data collection

Bruker APEXII CCD area-detector diffractometer	1691 independent reflections
Radiation source: fine-focus sealed tube	1379 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.037
T = 120 K	θ_{max} = 27.0º
φ and ω scans	θ_{min} = 3.1º
Absorption correction: multi-scan (SADABS; Bruker, 2005)	*h* = −15→15
T_{min} = 0.730, T_{max} = 0.828	*k* = −12→12

8276 measured reflections

$l = -14 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.065$

$S = 0.98$

1691 reflections

138 parameters

6 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

$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.44$ e Å^{-3}

$\Delta\rho_{min} = -0.33$ e Å^{-3}

Extinction correction: none

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.

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.0000	0.27554 (3)	0.7500	0.01072 (11)
O1	0.03285 (11)	0.42083 (13)	0.86619 (11)	0.0142 (3)
H11	0.0898 (11)	0.4670 (18)	0.8664 (17)	0.019 (6)*
H12	−0.0189 (14)	0.475 (2)	0.864 (2)	0.044 (8)*
O2	0.15591 (10)	0.29226 (13)	0.70290 (10)	0.0129 (3)
H21	0.1953 (16)	0.315 (2)	0.7545 (13)	0.032 (7)*
H22	0.184 (2)	0.2274 (19)	0.672 (2)	0.052 (9)*
O3	0.26260 (10)	−0.06943 (12)	1.12935 (10)	0.0145 (3)
O4	0.21890 (10)	0.15053 (12)	1.12590 (10)	0.0166 (3)
O5	−0.12732 (13)	0.60197 (15)	0.83875 (13)	0.0301 (4)
H51	−0.1494 (18)	0.6770 (14)	0.8598 (18)	0.033 (7)*
H52	−0.1726 (19)	0.580 (3)	0.7913 (18)	0.067 (10)*
N1	0.04499 (11)	0.11232 (14)	0.84534 (11)	0.0106 (3)
C1	0.21332 (13)	0.03194 (17)	1.08927 (14)	0.0119 (4)
C2	0.14678 (14)	0.01069 (17)	0.98899 (14)	0.0116 (4)

C3	0.13045 (14)	−0.11715 (17)	0.94398 (14)	0.0119 (4)
H3	0.1595	−0.1960	0.9778	0.014*
C4	0.07152 (14)	−0.12874 (17)	0.84950 (14)	0.0126 (4)
H4	0.0596	−0.2156	0.8180	0.015*
C5	0.03040 (13)	−0.01275 (17)	0.80161 (14)	0.0108 (4)
C7	0.10106 (14)	0.12224 (17)	0.93712 (14)	0.0117 (4)
H7	0.1100	0.2097	0.9683	0.014*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01160 (18)	0.00978 (17)	0.01056 (18)	0.000	−0.00259 (12)	0.000
O1	0.0113 (7)	0.0133 (7)	0.0177 (7)	0.0017 (5)	−0.0029 (5)	−0.0029 (5)
O2	0.0122 (6)	0.0148 (7)	0.0115 (7)	0.0004 (5)	−0.0030 (5)	−0.0024 (5)
O3	0.0155 (7)	0.0126 (6)	0.0151 (7)	−0.0005 (5)	−0.0059 (5)	0.0034 (5)
O4	0.0203 (7)	0.0133 (7)	0.0156 (7)	0.0013 (5)	−0.0064 (6)	−0.0043 (5)
O5	0.0286 (9)	0.0212 (8)	0.0392 (10)	0.0123 (6)	−0.0167 (7)	−0.0135 (7)
N1	0.0109 (8)	0.0106 (8)	0.0103 (8)	−0.0013 (5)	−0.0011 (6)	0.0005 (6)
C1	0.0101 (9)	0.0143 (9)	0.0113 (9)	−0.0019 (7)	0.0008 (7)	0.0014 (7)
C2	0.0108 (8)	0.0148 (9)	0.0092 (9)	−0.0002 (7)	0.0003 (7)	0.0005 (7)
C3	0.0110 (9)	0.0118 (9)	0.0128 (9)	0.0010 (6)	−0.0007 (7)	0.0020 (7)
C4	0.0132 (9)	0.0108 (9)	0.0140 (9)	−0.0006 (7)	0.0011 (7)	−0.0018 (7)
C5	0.0094 (8)	0.0124 (9)	0.0106 (9)	−0.0006 (6)	0.0009 (7)	−0.0007 (7)
C7	0.0110 (9)	0.0124 (9)	0.0118 (9)	−0.0014 (7)	0.0013 (7)	−0.0015 (7)

Geometric parameters (Å, °)

Ni1—O2^{i}	2.0622 (12)	O5—H52	0.837 (10)
Ni1—O2	2.0622 (12)	N1—C7	1.337 (2)
Ni1—N1^{i}	2.0706 (14)	N1—C5	1.356 (2)
Ni1—N1	2.0706 (14)	C1—C2	1.505 (2)
Ni1—O1	2.0782 (13)	C2—C7	1.388 (2)
Ni1—O1^{i}	2.0782 (13)	C2—C3	1.390 (2)
O1—H11	0.843 (9)	C3—C4	1.385 (2)
O1—H12	0.834 (10)	C3—H3	0.9500
O2—H21	0.833 (10)	C4—C5	1.380 (2)
O2—H22	0.834 (10)	C4—H4	0.9500
O3—C1	1.266 (2)	C5—C5^{i}	1.486 (3)
O4—C1	1.254 (2)	C7—H7	0.9500
O5—H51	0.834 (10)		
O2^{i}—Ni1—O2	170.87 (7)	C7—N1—C5	118.59 (14)
O2^{i}—Ni1—N1^{i}	89.51 (5)	C7—N1—Ni1	124.87 (11)
O2—Ni1—N1^{i}	97.57 (5)	C5—N1—Ni1	115.66 (12)
O2^{i}—Ni1—N1	97.57 (5)	O4—C1—O3	124.20 (16)
O2—Ni1—N1	89.51 (5)	O4—C1—C2	117.49 (15)
N1^{i}—Ni1—N1	78.63 (8)	O3—C1—C2	118.27 (15)
O2^{i}—Ni1—O1	84.53 (5)	C7—C2—C3	117.82 (16)

O2—Ni1—O1	89.21 (5)	C7—C2—C1	119.58 (15)
N1^{i}—Ni1—O1	170.17 (6)	C3—C2—C1	122.59 (15)
N1—Ni1—O1	94.39 (5)	C4—C3—C2	119.54 (15)
O2^{i}—Ni1—O1^{i}	89.21 (5)	C4—C3—H3	120.2
O2—Ni1—O1^{i}	84.53 (5)	C2—C3—H3	120.2
N1^{i}—Ni1—O1^{i}	94.39 (5)	C5—C4—C3	119.24 (16)
N1—Ni1—O1^{i}	170.17 (6)	C5—C4—H4	120.4
O1—Ni1—O1^{i}	93.34 (7)	C3—C4—H4	120.4
Ni1—O1—H11	121.0 (15)	N1—C5—C4	121.70 (16)
Ni1—O1—H12	106.4 (18)	N1—C5—C5^{i}	114.53 (10)
H11—O1—H12	108 (2)	C4—C5—C5^{i}	123.75 (10)
Ni1—O2—H21	109.3 (17)	N1—C7—C2	123.09 (15)
Ni1—O2—H22	119.7 (19)	N1—C7—H7	118.5
H21—O2—H22	109 (2)	C2—C7—H7	118.5
H51—O5—H52	104 (3)		
O2^{i}—Ni1—N1—C7	−99.70 (14)	C7—C2—C3—C4	1.0 (3)
O2—Ni1—N1—C7	74.51 (14)	C1—C2—C3—C4	−177.65 (16)
N1^{i}—Ni1—N1—C7	172.33 (18)	C2—C3—C4—C5	0.2 (3)
O1—Ni1—N1—C7	−14.65 (15)	C7—N1—C5—C4	0.2 (3)
O1^{i}—Ni1—N1—C7	127.1 (3)	Ni1—N1—C5—C4	169.99 (14)
O2^{i}—Ni1—N1—C5	91.22 (12)	C7—N1—C5—C5^{i}	−178.46 (17)
O2—Ni1—N1—C5	−94.57 (12)	Ni1—N1—C5—C5^{i}	−8.7 (2)
N1^{i}—Ni1—N1—C5	3.25 (9)	C3—C4—C5—N1	−0.9 (3)
O1—Ni1—N1—C5	176.26 (12)	C3—C4—C5—C5^{i}	177.6 (2)
O1^{i}—Ni1—N1—C5	−42.0 (4)	C5—N1—C7—C2	1.2 (3)
O4—C1—C2—C7	4.6 (3)	Ni1—N1—C7—C2	−167.62 (13)
O3—C1—C2—C7	−173.22 (16)	C3—C2—C7—N1	−1.8 (3)
O4—C1—C2—C3	−176.75 (16)	C1—C2—C7—N1	176.94 (15)
O3—C1—C2—C3	5.4 (3)		

Symmetry codes: (i) −*x*, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H52···O3^{ii}	0.837 (10)	2.178 (16)	2.9566 (19)	155 (3)
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O5—H51···O4^{iv}	0.834 (10)	1.913 (11)	2.7286 (19)	166 (2)
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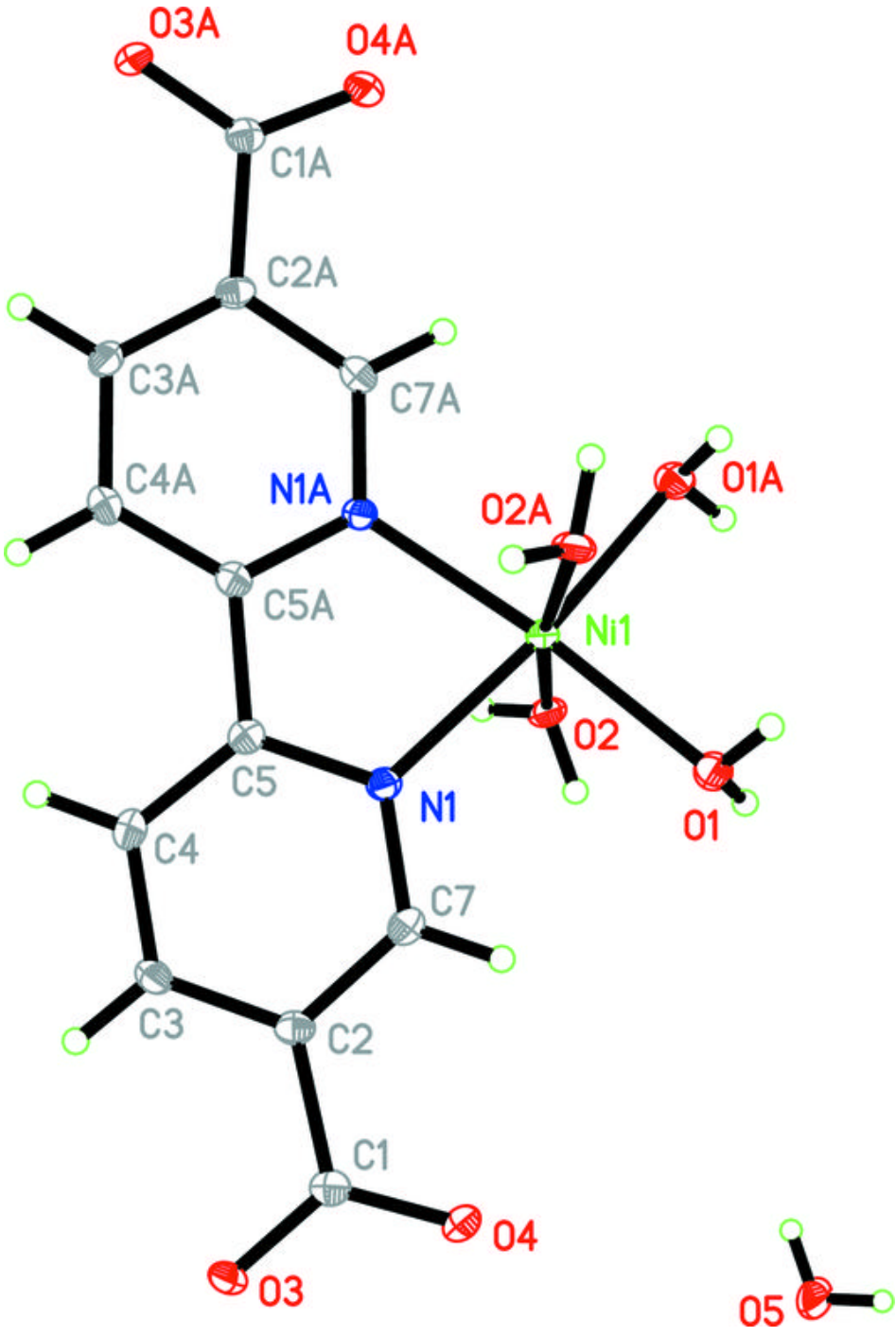
O1—H11···O4^{v}	0.843 (9)	2.650 (17)	3.1740 (18)	121.6 (16)
O1—H11···O3^{v}	0.843 (9)	2.097 (10)	2.9386 (18)	175.9 (19)
O1—H12···O5	0.834 (10)	1.861 (11)	2.688 (2)	171 (3)

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

Fig. 1


O3A
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C2A
C3A
C7A
C4A
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C5A
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O2
C5
N1
O1
C4
C7
C3
C2
C1
O4
O3
O5

Fig. 2