

Hexaaquamagnesium(II) bis(pyridinium-2,6-dicarboxylate)

Hoda Pasdar,^a Sanaz Heidari,^{a*} Hossein Aghabozorg^a and Behrouz Notash^b

^aDepartment of Chemistry, Islamic Azad University, North Tehran Branch, Tehran, Iran, and ^bDepartment of Chemistry, Shahid Beheshti University, G. C., Evin, Tehran 1983963113, Iran

Correspondence e-mail: heidari.sanaz3335@yahoo.com

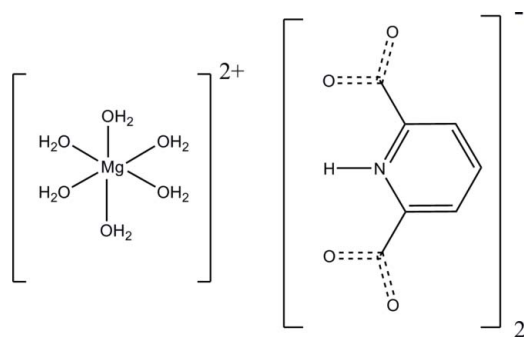
Received 11 October 2010; accepted 11 November 2010

Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.038; wR factor = 0.095; data-to-parameter ratio = 14.7.

In the title compound, $[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_7\text{H}_4\text{NO}_4)_2$, a single six-coordinate Mg^{2+} cation (site symmetry $2/m$) is bonded to six water molecules in a distorted octahedral geometry. The crystal packing between the complex cation and the zwitterionic organic anion (m symmetry) is stabilized by intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds and weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ interactions.

Related literature

For background to proton-transfer compounds, see: Aghabozorg *et al.* (2008). For related structures, see: Aghabozorg *et al.* (2005); Grossel *et al.* (2006); Ptasiwicz-Bak & Leciejewicz (2003); Dale *et al.* (2003); Yang *et al.* (2005); Kariuki & Jones (1989)



Experimental

Crystal data

$[\text{Mg}(\text{H}_2\text{O})_6](\text{C}_7\text{H}_4\text{NO}_4)_2$

$M_r = 464.63$

Monoclinic, $C2/m$
 $a = 13.432$ (3) Å
 $b = 11.108$ (2) Å
 $c = 6.5845$ (13) Å
 $\beta = 92.79$ (3)°
 $V = 981.3$ (3) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.17$ mm⁻¹
 $T = 298$ K
 $0.35 \times 0.30 \times 0.15$ mm

Data collection

Stoe IPDS II diffractometer
 Absorption correction: numerical
 ($X\text{-RED}$ and $X\text{-SHAPE}$;
 Stoe & Cie, 2005)
 $T_{\text{min}} = 0.940$, $T_{\text{max}} = 0.973$

5499 measured reflections
 1383 independent reflections
 1178 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.095$
 $S = 1.12$
 1383 reflections
 94 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3}-\text{H3}\cdots\text{O1}$	0.862 (19)	1.834 (19)	2.6940 (14)	174.6 (19)
$\text{O4}-\text{H4}\cdots\text{O2}$	0.85 (2)	1.93 (2)	2.7758 (14)	171 (2)
$\text{O5}-\text{H5}\cdots\text{O2}^{\text{i}}$	0.89 (2)	1.92 (2)	2.7960 (14)	167.5 (19)
$\text{C1}-\text{H1}\cdots\text{O5}^{\text{ii}}$	0.93	2.58	3.308 (3)	136

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

Data collection: $X\text{-AREA}$ (Stoe & Cie, 2005); cell refinement: $X\text{-AREA}$; data reduction: $X\text{-AREA}$; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: $\text{ORTEP-3 for Windows}$ (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

The authors are grateful to the Islamic Azad University, North Branch, for financial support of this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JJ2069).

References

- Aghabozorg, H., Akbari Saei, A. & Ramezanipour, F. (2005). *Acta Cryst.* **E61**, o3242–o3244.
 Aghabozorg, H., Manteghi, F. & Sheshmani, S. (2008). *J. Iran. Chem. Soc.* **5**, 184–227.
 Dale, S. H., Elsegood, M. R. J. & Kainth, S. (2003). *Acta Cryst.* **C59**, m505–m508.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
 Grossel, M. C., Dwyer, A. N., Hursthouse, M. B. & Orton, J. B. (2006). *CrystEngComm*, **8**, 123–128.
 Kariuki, B. M. & Jones, W. (1989). *Acta Cryst.* **C45**, 1297–1299.
 Ptasiwicz-Bak, H. & Leciejewicz, J. (2003). *J. Coord. Chem.* **56**, 173–180.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Stoe & Cie (2005). $X\text{-AREA}$, $X\text{-RED}$ and $X\text{-SHAPE}$. Stoe & Cie, Darmstadt, Germany.
 Yang, Q., Gao, S. & Huo, L.-H. (2005). *Acta Cryst.* **E61**, m277–m278.

supporting information

Acta Cryst. (2010). E66, m1581 [https://doi.org/10.1107/S1600536810046696]

Hexaaquamagnesium(II) bis(pyridinium-2,6-dicarboxylate)**Hoda Pasdar, Sanaz Heidari, Hossein Aghabozorg and Behrouz Notash****S1. Comment**

Pyridine-2,6-dicarboxylic acid is commonly used as proton donor in proton transfer systems (Aghabozorg *et al.* 2008). It has been reported that the carboxylate groups are deprotonated and the pyridine ring is protonated in compounds containing pyridine-2,6-dicarboxylic acid (Aghabozorg *et al.* 2005; Grossel *et al.* 2006). In addition, the formation of a six-coordinated magnesium (II) ion by water molecules in aqueous solution in the presence of poly carboxylic acids has been observed (Dale *et al.* 2003; Ptasiwicz-Bak & Leciejewicz 2003; Yang *et al.* 2005). The structure of hexa-aqua-magnesium(II) pyrazine-2,6-dicarboxylate, $[\text{Mg}(\text{H}_2\text{O})_6][\text{pz-2,6-dc}]$, has also been reported which exhibits hydrogen bonding between the cationic magnesium species and a pyrazine-2,6-dicarboxylate anion (Ptasiwicz-Bak & Leciejewicz 2003).

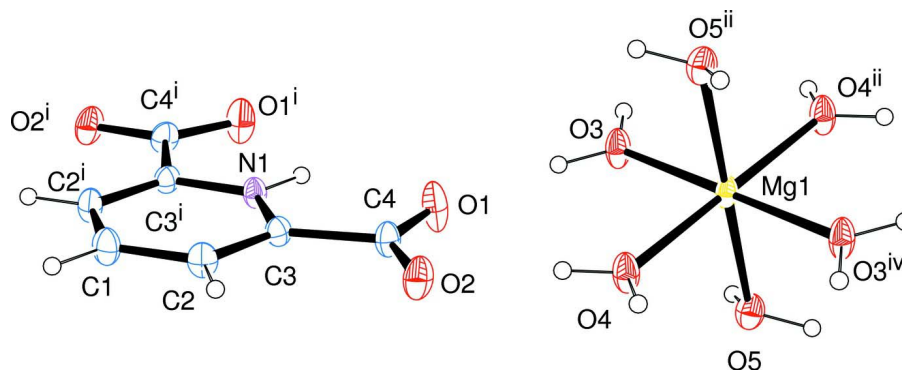
In the title compound, $[\text{Mg}(\text{H}_2\text{O})_6][\text{pyH-2,6-dc}]_2$, the cation is comprised of a six-coordinate Mg^{II} ion bound by water molecules in a distorted octahedral geometry. The dianion is comprised of a pyridine-2,6-dicarboxylic acid group (Fig. 1). Bond lengths and angles for $\text{Mg}-\text{O}$ are in normal ranges. Crystal packing is stabilized by $\text{O}-\text{H}\cdots\text{O}$ intra and intermolecular hydrogen bonds and weak $\text{C}-\text{H}\cdots\text{O}$ intermolecular hydrogen bond interactions with the coordinated water molecules (Fig. 2). The pyridine ring in the dianion is protonated and the two carboxylic acid groups are deprotonated forming a proton transfer fragment.

S2. Experimental

A solution of pyridine-2,6-dicarboxylic acid (pydcH_2) (0.1671 g, 1 mmol) in ethanol (20 ml) was added to a solution of pyridazine (pydz) (0.072 ml, 1 mmol) in ethanol (8 ml) and stirred for 2 hrs. Then an aqueous solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1282 g, 0.5 mmol) was added to mixture of pydcH_2 - pydz and stirred for 1 h. 1 mL DMSO was then added to the mixture to clear the solution and stirred for more 2 hrs. Slow evaporation of the resulting solution gave colorless crystals of the title compound after three weeks which were suitable for X-ray analysis (decomposition $> 260^\circ\text{C}$).

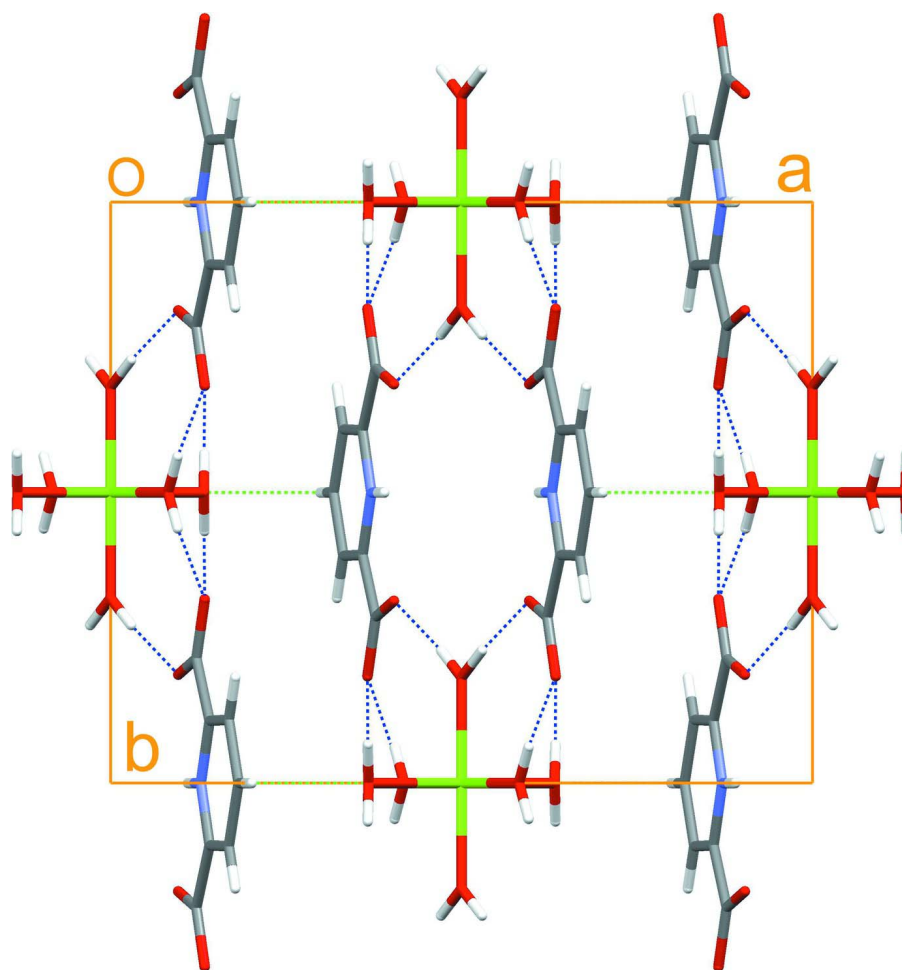
S3. Refinement

The hydrogen atoms from the water molecules and pyridinium group were found in a difference Fourier map and refined isotropically without restraint. The $\text{C}-\text{H}$ protons of the aromatic ring were positioned geometrically and refined as riding atoms, with $\text{C}-\text{H} = 0.93\text{\AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

**Figure 1**

The molecular structure of $[\text{Mg}(\text{H}_2\text{O})_6][\text{pyH-2,6-dc}]_2$ with displacement ellipsoids drawn at 30% probability level.

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

**Figure 2**

The packing diagram of $[\text{Mg}(\text{H}_2\text{O})_6][\text{pyH-2,6-dc}]_2$ viewed down the c -axis. The intra and intermolecular $\text{O}-\text{H}\cdots\text{O}$ and intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds are shown as blue and green dashed lines, respectively.

Hexaaquamagnesium(II) bis(pyridinium-2,6-dicarboxylate)

Crystal data

[Mg(H₂O)₆](C₇H₄NO₄)₂ $M_r = 464.63$ Monoclinic, $C2/m$ Hall symbol: $-C\ 2y$ $a = 13.432\ (3)\ \text{\AA}$ $b = 11.108\ (2)\ \text{\AA}$ $c = 6.5845\ (13)\ \text{\AA}$ $\beta = 92.79\ (3)^\circ$ $V = 981.3\ (3)\ \text{\AA}^3$ $Z = 2$ $F(000) = 484.0$ $D_x = 1.572\ \text{Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1383 reflections

 $\theta = 2.4\text{--}29.1^\circ$ $\mu = 0.17\ \text{mm}^{-1}$ $T = 298\ \text{K}$

Plate, colorless

 $0.35 \times 0.30 \times 0.15\ \text{mm}$

Data collection

Stoe IPDS II

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: $0.15\ \text{pixels mm}^{-1}$

rotation method scans

Absorption correction: numerical

 $(X\text{-RED and X-SHAPE; Stoe \& Cie, 2005)}$ $T_{\min} = 0.940, T_{\max} = 0.973$

5499 measured reflections

1383 independent reflections

1178 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.031$ $\theta_{\max} = 29.1^\circ, \theta_{\min} = 2.4^\circ$ $h = -17 \rightarrow 18$ $k = -14 \rightarrow 15$ $l = -9 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.038$ $wR(F^2) = 0.095$ $S = 1.12$

1383 reflections

94 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 atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 0.5177P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.33\ \text{e \AA}^{-3}$ $\Delta\rho_{\min} = -0.18\ \text{e \AA}^{-3}$

Special details

Experimental. shape of crystal determined optically**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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Mg1	0.5000	0.0000	0.0000	0.0249 (2)
O1	0.40364 (11)	0.31353 (9)	0.27234 (16)	0.0499 (3)

O2	0.36594 (9)	0.18375 (8)	0.51657 (15)	0.0396 (3)
O3	0.5000	0.18182 (12)	0.0000	0.0360 (3)
O4	0.41819 (12)	0.0000	0.2566 (2)	0.0357 (3)
O5	0.36739 (11)	0.0000	-0.1931 (2)	0.0341 (3)
N1	0.37142 (12)	0.5000	0.4931 (2)	0.0257 (3)
C1	0.31770 (16)	0.5000	0.8796 (3)	0.0347 (4)
H1	0.2989	0.5000	1.0137	0.042*
C2	0.33156 (11)	0.39121 (12)	0.78070 (19)	0.0312 (3)
H2	0.3225	0.3186	0.8476	0.037*
C3	0.35898 (9)	0.39277 (10)	0.58164 (18)	0.0253 (3)
C4	0.37779 (11)	0.28571 (11)	0.4447 (2)	0.0310 (3)
H3	0.4708 (14)	0.2281 (19)	0.084 (3)	0.053 (5)*
H4	0.4046 (15)	0.0617 (19)	0.327 (3)	0.057 (6)*
H5	0.3664 (16)	0.0661 (19)	-0.270 (3)	0.065 (6)*
H1A	0.3899 (19)	0.5000	0.366 (4)	0.046 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0367 (5)	0.0173 (4)	0.0211 (4)	0.000	0.0062 (3)	0.000
O1	0.0892 (9)	0.0278 (5)	0.0351 (5)	0.0102 (5)	0.0267 (6)	-0.0011 (4)
O2	0.0626 (7)	0.0192 (4)	0.0374 (5)	0.0041 (4)	0.0054 (5)	0.0011 (4)
O3	0.0602 (10)	0.0177 (6)	0.0315 (7)	0.000	0.0172 (6)	0.000
O4	0.0566 (9)	0.0226 (6)	0.0296 (7)	0.000	0.0179 (6)	0.000
O5	0.0467 (8)	0.0295 (7)	0.0262 (6)	0.000	0.0034 (6)	0.000
N1	0.0353 (8)	0.0203 (7)	0.0220 (6)	0.000	0.0081 (6)	0.000
C1	0.0486 (12)	0.0344 (10)	0.0217 (8)	0.000	0.0080 (7)	0.000
C2	0.0422 (8)	0.0253 (6)	0.0265 (6)	0.0000 (5)	0.0059 (5)	0.0048 (5)
C3	0.0303 (6)	0.0192 (5)	0.0267 (5)	0.0018 (4)	0.0036 (4)	0.0007 (4)
C4	0.0410 (7)	0.0210 (6)	0.0312 (6)	0.0050 (5)	0.0048 (5)	-0.0027 (5)

Geometric parameters (Å, °)

Mg1—O3 ⁱ	2.0197 (14)	O5—H5	0.89 (2)
Mg1—O3	2.0197 (14)	N1—C3 ⁱⁱ	1.3401 (13)
Mg1—O4 ⁱ	2.0601 (15)	N1—C3	1.3401 (13)
Mg1—O4	2.0601 (15)	N1—H1A	0.89 (3)
Mg1—O5 ⁱ	2.1375 (16)	C1—C2	1.3897 (16)
Mg1—O5	2.1375 (16)	C1—C2 ⁱⁱ	1.3897 (16)
O1—C4	1.2422 (17)	C1—H1	0.9300
O2—C4	1.2406 (16)	C2—C3	1.3788 (17)
O3—H3	0.862 (19)	C2—H2	0.9300
O4—H4	0.85 (2)	C3—C4	1.5208 (17)
O3 ⁱ —Mg1—O3	180.0	Mg1—O5—H5	109.1 (13)
O3 ⁱ —Mg1—O4 ⁱ	90.0	C3 ⁱⁱ —N1—C3	125.46 (15)
O3—Mg1—O4 ⁱ	90.0	C3 ⁱⁱ —N1—H1A	117.27 (8)
O3 ⁱ —Mg1—O4	90.0	C3—N1—H1A	117.27 (8)

O3—Mg1—O4	90.0	C2—C1—C2 ⁱⁱ	120.82 (17)
O4 ⁱ —Mg1—O4	180.00 (8)	C2—C1—H1	119.6
O3 ⁱ —Mg1—O5 ⁱ	90.0	C2 ⁱⁱ —C1—H1	119.6
O3—Mg1—O5 ⁱ	90.0	C3—C2—C1	118.87 (12)
O4 ⁱ —Mg1—O5 ⁱ	91.46 (6)	C3—C2—H2	120.6
O4—Mg1—O5 ⁱ	88.54 (6)	C1—C2—H2	120.6
O3 ⁱ —Mg1—O5	90.0	N1—C3—C2	117.99 (12)
O3—Mg1—O5	90.0	N1—C3—C4	114.17 (11)
O4 ⁱ —Mg1—O5	88.54 (6)	C2—C3—C4	127.84 (11)
O4—Mg1—O5	91.46 (6)	O2—C4—O1	128.49 (12)
O5 ⁱ —Mg1—O5	180.00 (8)	O2—C4—C3	117.37 (12)
Mg1—O3—H3	126.6 (13)	O1—C4—C3	114.14 (11)
Mg1—O4—H4	125.5 (14)		
C2 ⁱⁱ —C1—C2—C3	-0.3 (3)	N1—C3—C4—O2	-178.85 (14)
C3 ⁱⁱ —N1—C3—C2	-0.3 (3)	C2—C3—C4—O2	1.3 (2)
C3 ⁱⁱ —N1—C3—C4	179.77 (12)	N1—C3—C4—O1	1.23 (19)
C1—C2—C3—N1	0.3 (2)	C2—C3—C4—O1	-178.66 (14)
C1—C2—C3—C4	-179.83 (15)		

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O3—H3 \cdots O1	0.862 (19)	1.834 (19)	2.6940 (14)	174.6 (19)
O4—H4 \cdots O2	0.85 (2)	1.93 (2)	2.7758 (14)	171 (2)
O5—H5 \cdots O2 ⁱⁱⁱ	0.89 (2)	1.92 (2)	2.7960 (14)	167.5 (19)
C1—H1 \cdots O5 ^{iv}	0.93	2.58	3.308 (3)	136

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