

trans-Diaquabis(1*H* imidazolium-4,5-dicarboxylato- $\kappa^2 O^4, O^5$)magnesium

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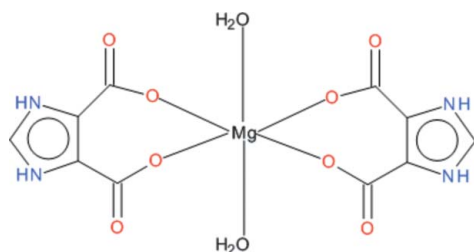
Received 18 April 2012; accepted 20 April 2012

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}—\text{C}) = 0.002$ Å; R factor = 0.033; wR factor = 0.101; data-to-parameter ratio = 13.9.

The title compound, $[\text{Mg}(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$, consists of centrosymmetric neutral monomers in which two *O,O'*-bidentate imidazolium-4,5-dicarboxylate ligands are bonded to the Mg^{II} ion. One of the carboxyl protons is transferred to the N atom of the imidazole ring. The octahedral metal-ion coordination is completed by two *trans* water O atoms. In the crystal, molecules are linked by $\text{N}—\text{H}\cdots(\text{O},\text{O})$ and $\text{O}—\text{H}\cdots\text{O}$ hydrogen bonds.

Related literature

For the crystal structures of two Ca^{II} complexes with imidazole-4,5-dicarboxylate and aqua ligands, see: Starosta *et al.* (2006) and for the structure of a Ba^{II} complex, see: Starosta *et al.* (2007).



Experimental

Crystal data

$[\text{Mg}(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$
 $M_r = 370.53$
 Monoclinic, $P2_1/c$
 $a = 7.2545$ (15) Å
 $b = 13.847$ (3) Å
 $c = 6.9975$ (14) Å
 $\beta = 115.46$ (3)°

$V = 634.6$ (2) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.22$ mm^{−1}
 $T = 293$ K
 $0.22 \times 0.21 \times 0.15$ mm

Data collection

Kuma KM-4 four-circle diffractometer
 Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2008)
 $T_{\min} = 0.957$, $T_{\max} = 0.970$
 1955 measured reflections

1821 independent reflections
 1439 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.008$
 3 standard reflections every 200 reflections
 intensity decay: 0.6%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.101$
 $S = 1.04$
 1821 reflections
 131 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.42$ e Å^{−3}
 $\Delta\rho_{\min} = -0.28$ e Å^{−3}

Table 1

Selected bond lengths (Å).

Mg1—O3	2.0212 (10)	Mg1—O5	2.0553 (12)
Mg1—O1	2.0297 (12)		

Table 2

Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N1—H1 ⁱ ⋯O2 ⁱ	0.92 (3)	1.85 (3)	2.7711 (16)	175 (2)
N1—H1 ⁱ ⋯O1 ⁱ	0.92 (3)	2.58 (2)	3.1446 (16)	119.6 (18)
N2—H3 ⁱⁱ ⋯O3 ⁱⁱ	0.86	2.51	3.1192 (17)	129
N2—H3 ⁱⁱ ⋯O5 ⁱⁱ	0.86	2.55	3.3678 (19)	159
O5—H51 ⁱⁱⁱ ⋯O2 ⁱⁱⁱ	0.86 (3)	1.94 (3)	2.7936 (19)	176 (2)
O5—H52 ^{iv} ⋯O4 ^{iv}	0.82 (3)	1.90 (3)	2.7108 (16)	167 (3)

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

Data collection: *KM-4 Software* (Kuma, 1996); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Kuma, 2001); 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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6745).

References

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 Starosta, W., Leciejewicz, J., Premkumar, T. & Govindarajan, S. (2007). *J. Coord. Chem.* **60**, 313–318.

supporting information

Acta Cryst. (2012). E68, m688 [https://doi.org/10.1107/S1600536812017667]

***trans*-Diaquabis(1*H* imidazolium-4,5-dicarboxylato- κ^2 O⁴,O⁵)magnesium**

Katarzyna Łuczyńska-Szymczak, Wojciech Starosta and Janusz Leciejewicz

S1. Comment

The monoclinic structure of the title compound is built of monomeric molecules with Mg^{II} cation in an inversion centre coordinated by two equatorial imidazole-4,5-dicarboxylate ligands which use two carboxylate O atoms, each donated by a different carboxylate group (Fig.1). Hydrogen atom, clearly visible on a Fourier map, attached to the heteroring-N atom maintains charge balance. Two aqua O atoms at axial positions complete a slightly distorted octahedral coordination geometry of the Mg^{II} cation (Table 1). The imidazole ring is almost planar with r.m.s. deviation of 0.0033 (1) Å. The C6/O1/O2 and C7/O3/O4 groups make with the ring dihedral angles of 32.2 (2)° and 8.8 (1)°, respectively. Hydrogen bonds shorter than 3 Å (D...A separation) in which coordinated water O atoms act as donors and carboxylato O atoms in adjacent monomers as acceptors join the monomers into molecular columns. The latter are interconnected by hydrogen bonds in which protonated nitrogen atoms are donors and carboxylato O atoms are acceptors (see, Table 2 and Fig.2). A different coordination mode was reported in the structure of a Ca^{II} monomeric complex with the title ligand: the metal ion, besides four water O atoms, is coordinated by two N,O bonding moieties donated by two title ligand molecules. The second carboxylate O atom of this moiety remains protonated and forms a short hydrogen bond of 2.511 (2) Å to the O atom in the adjacent carboxylic group (Starosta *et al.*, 2006). The polymeric structure of a Ba^{II} complex with the title ligand can be described as built of monomeric structural units in which a Ba^{II} ion, like in the Ca^{II} complex, is coordinated by two ligands *via* N,O chelating sites. Their second O atoms are protonated and make a short hydrogen bond of 2.495 (2) Å to the O atoms in the adjacent carboxylate group (Starosta *et al.*, 2007).

S2. Experimental

1 mmol of magnesium(II) nitrate hexahydrate and 2 mmol of imidazole-4,5-dicarboxylic acid (Aldrich) were dissolved in 20 ml of doubly distilled water, stirred for two hours, closed in a pressure vessel and kept at 363 K for three days. Then, the vessel was slowly cooled to room temperature. The deposited colourless blocks were washed with cold distilled water and dried in the air.

S3. Refinement

Water and attached to nitrogen hydrogen atoms were located in a difference map and refined isotropically, while the H atom attached to imidazole C atom was located at a calculated position and treated as riding on the parent atom with C—H=0.93 Å and $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$.

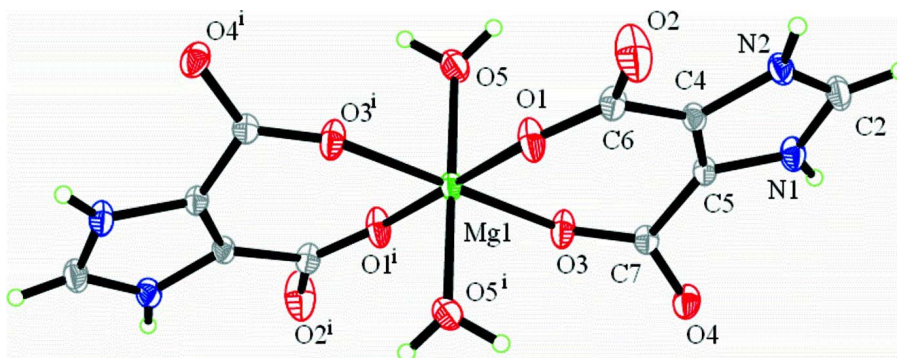


Figure 1

A molecule of the title compound with 50% probability displacement ellipsoids. Symmetry code: (i) $-x + 1, -y + 2, -z + 1$.

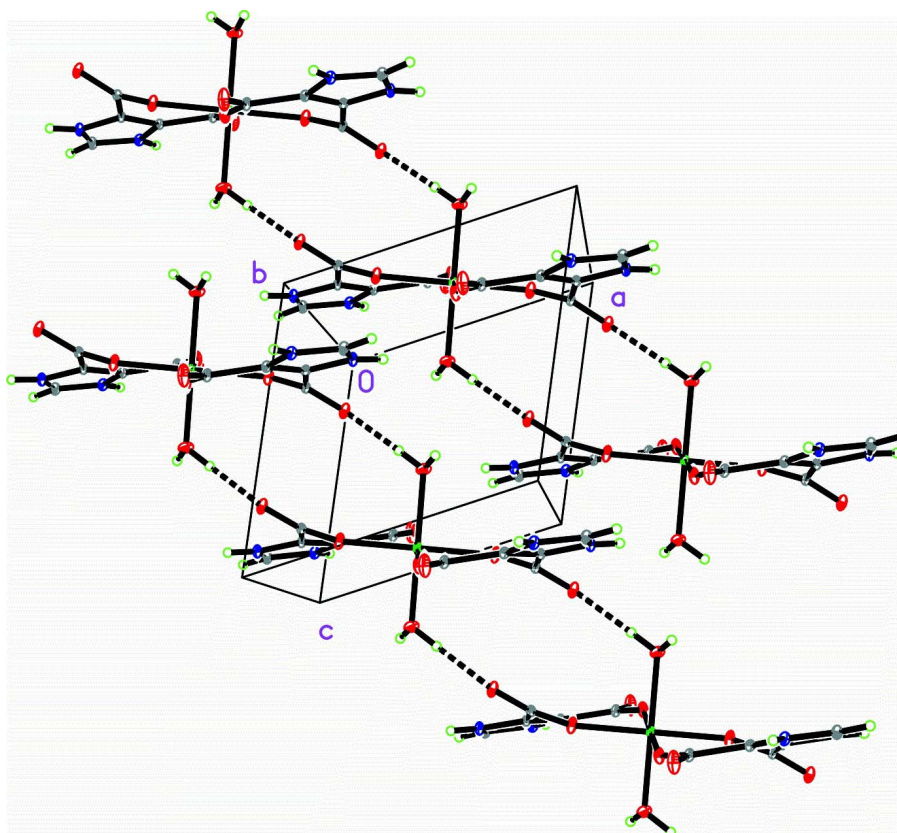


Figure 2

Packing diagram of the structure.

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Crystal data

$[\text{Mg}(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$

$M_r = 370.53$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 7.2545(15)\text{ \AA}$

$b = 13.847(3)\text{ \AA}$

$c = 6.9975(14)\text{ \AA}$

$\beta = 115.46(3)^\circ$

$V = 634.6(2)\text{ \AA}^3$

$Z = 2$

$F(000) = 380$

$D_x = 1.939\text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 6\text{--}15^\circ$
 $\mu = 0.22 \text{ mm}^{-1}$

$T = 293 \text{ K}$
 Blocks, colourless
 $0.22 \times 0.21 \times 0.15 \text{ mm}$

Data collection

Kuma KM-4 four-circle
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 profile data from $\omega/2\theta$ scans
 Absorption correction: analytical
 (*CrysAlis RED*; Oxford Diffraction, 2008)
 $T_{\min} = 0.957$, $T_{\max} = 0.970$
 1955 measured reflections

1821 independent reflections
 1439 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.008$
 $\theta_{\max} = 30.1^\circ$, $\theta_{\min} = 2.9^\circ$
 $h = -9 \rightarrow 0$
 $k = 0 \rightarrow 19$
 $l = -8 \rightarrow 9$
 3 standard reflections every 200 reflections
 intensity decay: 0.6%

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.101$
 $S = 1.04$
 1821 reflections
 131 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
 $w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 0.2647P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.42 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e \AA}^{-3}$

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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Mg1	0.5000	1.0000	0.5000	0.01407 (15)
O2	1.12854 (15)	1.02751 (7)	0.85653 (17)	0.0232 (2)
O1	0.80572 (15)	1.02280 (7)	0.62178 (18)	0.0232 (2)
N2	1.18660 (17)	0.84179 (8)	0.72988 (19)	0.0192 (2)
H3	1.2942	0.8756	0.7557	0.023*
N1	0.98697 (17)	0.71976 (8)	0.67452 (18)	0.0179 (2)
O5	0.5127 (2)	1.02541 (9)	0.79479 (18)	0.0302 (3)
C4	0.99878 (18)	0.87861 (9)	0.69967 (19)	0.0143 (2)
C5	0.87167 (19)	0.80067 (8)	0.6632 (2)	0.0142 (2)
C6	0.97418 (19)	0.98431 (9)	0.7277 (2)	0.0145 (2)
C2	1.1754 (2)	0.74620 (10)	0.7128 (2)	0.0206 (3)

C7	0.65335 (19)	0.78744 (9)	0.6267 (2)	0.0170 (2)
H2	1.285 (3)	0.7067 (15)	0.725 (4)	0.035 (6)*
H51	0.624 (4)	1.0122 (17)	0.904 (4)	0.046 (7)*
O3	0.54299 (15)	0.86069 (7)	0.59542 (18)	0.0233 (2)
O4	0.59912 (18)	0.70322 (8)	0.6313 (2)	0.0367 (3)
H52	0.464 (4)	1.075 (2)	0.820 (4)	0.050 (7)*
H1	0.942 (4)	0.6569 (18)	0.665 (4)	0.045 (6)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0116 (3)	0.0123 (3)	0.0169 (3)	0.0021 (2)	0.0048 (2)	0.0014 (2)
O2	0.0148 (5)	0.0144 (4)	0.0315 (5)	−0.0017 (3)	0.0017 (4)	−0.0022 (4)
O1	0.0128 (5)	0.0144 (4)	0.0346 (6)	0.0016 (3)	0.0028 (4)	0.0040 (4)
N2	0.0121 (5)	0.0174 (5)	0.0267 (6)	0.0012 (4)	0.0070 (4)	0.0018 (4)
N1	0.0163 (5)	0.0119 (5)	0.0233 (5)	0.0027 (4)	0.0064 (4)	0.0002 (4)
O5	0.0307 (6)	0.0379 (6)	0.0189 (5)	0.0178 (5)	0.0077 (4)	−0.0015 (4)
C4	0.0113 (5)	0.0128 (5)	0.0175 (5)	0.0011 (4)	0.0049 (4)	0.0018 (4)
C5	0.0132 (5)	0.0103 (5)	0.0174 (5)	0.0017 (4)	0.0051 (4)	0.0014 (4)
C6	0.0133 (6)	0.0107 (5)	0.0191 (6)	−0.0008 (4)	0.0065 (4)	0.0016 (4)
C2	0.0159 (6)	0.0182 (6)	0.0261 (6)	0.0052 (4)	0.0076 (5)	0.0011 (5)
C7	0.0132 (5)	0.0132 (5)	0.0221 (6)	−0.0005 (4)	0.0053 (4)	0.0031 (4)
O3	0.0156 (5)	0.0152 (4)	0.0393 (6)	0.0037 (3)	0.0120 (4)	0.0066 (4)
O4	0.0217 (5)	0.0142 (5)	0.0715 (9)	−0.0022 (4)	0.0177 (6)	0.0077 (5)

Geometric parameters ($\text{\AA}$, $^\circ$)

Mg1—O3	2.0212 (10)	N1—C2	1.3266 (18)
Mg1—O3 ⁱ	2.0212 (10)	N1—C5	1.3798 (15)
Mg1—O1 ⁱ	2.0297 (12)	N1—H1	0.92 (3)
Mg1—O1	2.0297 (12)	O5—H51	0.86 (3)
Mg1—O5	2.0553 (12)	O5—H52	0.82 (3)
Mg1—O5 ⁱ	2.0553 (12)	C4—C5	1.3703 (16)
O2—C6	1.2477 (16)	C4—C6	1.4974 (17)
O1—C6	1.2442 (16)	C5—C7	1.5032 (18)
N2—C2	1.3283 (18)	C2—H2	0.94 (2)
N2—C4	1.3833 (16)	C7—O4	1.2355 (16)
N2—H3	0.8600	C7—O3	1.2517 (15)
O3—Mg1—O3 ⁱ	180.0	C5—N1—H1	125.1 (16)
O3—Mg1—O1 ⁱ	88.62 (4)	Mg1—O5—H51	118.4 (18)
O3 ⁱ —Mg1—O1 ⁱ	91.38 (4)	Mg1—O5—H52	121.3 (17)
O3—Mg1—O1	91.38 (4)	H51—O5—H52	108 (2)
O3 ⁱ —Mg1—O1	88.62 (4)	C5—C4—N2	106.13 (11)
O1 ⁱ —Mg1—O1	180.0	C5—C4—C6	133.29 (11)
O3—Mg1—O5	84.14 (5)	N2—C4—C6	120.34 (11)
O3 ⁱ —Mg1—O5	95.86 (5)	C4—C5—N1	106.62 (11)
O1 ⁱ —Mg1—O5	90.99 (6)	C4—C5—C7	134.67 (11)

O1—Mg1—O5	89.01 (6)	N1—C5—C7	118.64 (10)
O3—Mg1—O5 ⁱ	95.87 (5)	O1—C6—O2	124.86 (12)
O3 ⁱ —Mg1—O5 ⁱ	84.13 (5)	O1—C6—C4	118.85 (11)
O1 ⁱ —Mg1—O5 ⁱ	89.01 (6)	O2—C6—C4	116.28 (11)
O1—Mg1—O5 ⁱ	90.99 (6)	N1—C2—N2	108.12 (11)
O5—Mg1—O5 ⁱ	180.0	N1—C2—H2	128.0 (13)
C6—O1—Mg1	143.10 (9)	N2—C2—H2	123.9 (13)
C2—N2—C4	109.60 (11)	O4—C7—O3	125.63 (13)
C2—N2—H3	125.2	O4—C7—C5	115.75 (12)
C4—N2—H3	125.2	O3—C7—C5	118.62 (11)
C2—N1—C5	109.51 (11)	C7—O3—Mg1	145.83 (9)
C2—N1—H1	125.3 (15)		

Symmetry code: (i) $-x+1, -y+2, -z+1$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ O2 ⁱⁱ	0.92 (3)	1.85 (3)	2.7711 (16)	175 (2)
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N2—H3 $\cdots$ O5 ⁱⁱⁱ	0.86	2.55	3.3678 (19)	159
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O5—H52 $\cdots$ O4 ^v	0.82 (3)	1.90 (3)	2.7108 (16)	167 (3)

Symmetry codes: (ii) $-x+2, y-1/2, -z+3/2$; (iii) $x+1, y, z$; (iv) $-x+2, -y+2, -z+2$; (v) $-x+1, y+1/2, -z+3/2$.