metal-organic compounds

Bis(μ-pyridine-2,4-dicarboxylato)-κ³N,O²:O²;κ³O²:N,O²-bis[triaqua-magnesium(II)]

Qing-Fu Zhang,* Dan-Dan Han, Jian-Dong Pang and Ning-Ning Meng

College of Chemistry and Chemical Engineering, Liaocheng University, Shandong 252059, People's Republic of China
Correspondence e-mail: zhangqingfu@foxmail.com

In the title centrosymmetric Mg^{II} complex, $[Mg_2(C_7H_3NO_4)_2(H_2O)_6]$, each Mg cation is N,O-chelated by a pyridine-2,4-dicarboxylate dianion and is coordinated by three water molecules. A carboxylate O atom from the neighboring pyridine-2,4-dicarboxylate dianion bridges the Mg cation to complete the $MgNO_5$ distorted octahedral coordination geometry. The dinuclear complex molecules are linked by intermolecular O—H···O hydrogen bonding, forming a three-dimensional supramolecular structure.

Related literature

For the applications of Mg complexes, see: Davies *et al.* (2007); Dinca & Long (2005).
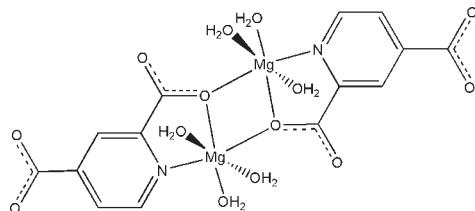
Experimental

Crystal data

$[Mg_2(C_7H_3NO_4)_2(H_2O)_6]$
M_r = 486.92
Orthorhombic, $Pbca$
a = 7.9221 (8) Å
b = 12.0951 (12) Å
c = 20.2989 (18) Å

V = 1945.0 (3) Å³
Z = 4
Mo $K\alpha$ radiation
μ = 0.21 mm⁻¹
T = 293 K
0.25 × 0.18 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.951, T_{max} = 0.970

8884 measured reflections
1719 independent reflections
1289 reflections with $I > 2\sigma(I)$
R_{int} = 0.042

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.100
S = 1.06
1719 reflections

145 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å⁻³
$\Delta\rho_{min}$ = −0.30 e Å⁻³

Table 1
Selected bond lengths (Å).

Mg1—N1	2.2202 (19)	Mg1—O5	2.0953 (19)
Mg1—O1	2.1011 (19)	Mg1—O6	2.017 (2)
Mg1—O1^i	2.0613 (16)	Mg1—O7	2.033 (2)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···O4^{ii}	0.87	1.80	2.668 (3)	172
O5—H5B···O2^{iii}	0.86	2.12	2.834 (3)	140
O6—H6A···O3^{iv}	0.87	1.73	2.576 (3)	163
O6—H6B···O5^{v}	0.87	2.07	2.880 (2)	154
O7—H7A···O4^{vi}	0.86	1.89	2.745 (2)	174
O7—H7B···O4^{vii}	0.86	2.02	2.857 (3)	166

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; 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*.

References

Davies, R. P., Less, R. J., Lickiss, P. D. & White, A. J. P. (2007). *Dalton Trans.* pp. 2528–2535.
Dinca, M. & Long, J. R. (2005). *J. Am. Chem. Soc.* **127**, 9376–9377.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Siemens. (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

supporting information

Bis(*μ*-pyridine-2,4-dicarboxylato)-*κ*^{3}*N,O*^{2}:*O*^{2};*κ*^{3}*O*^{2}:*N,O*^{2}-bis[triaqua-magnesium(II)]

Qing-Fu Zhang, Dan-Dan Han, Jian-Dong Pang and Ning-Ning Meng

S1. Comment

Magnesium(II) complexes have been extensively studied in recent year due to their wide application in synthesis of inorganic materials, catalysis of organic reactions and storage of hydrogen (Dinca & Long, 2005). In order to explore the relationship between these applications and their structures, a series of magnesium(II) complexes have been prepared and structural characterized (Davies *et al.*, 2007). To expand research in this area, here we report a dinuclear magnesium(II) complex.

As shown in Fig.1, each magnesium(II) ion in the title complex is coordinated by two carboxyl O atoms, one pyridyl N atom and three water molecules, forming a distorted octahedral geometry (axial angle, O7—Mg1—O5 = 173.33 (9)°). Interestingly, the two adjacent magnesium(II) ions are linked by two μ_2-carboxylate O atoms to form a dinuclear strucutre.

In the crystal strucutre, these dimeric molecules are linked by intermolecular O—H···O H-bonding interactions into a three-dimensional framework (Fig.2).

S2. Experimental

A mixture of pyridine-2,4-dicarboxylic acid (16.7 mg, 0.10 mmol) and magnesium chloride hexahydrate (20.3 mg, 0.10 mmol) in 5 ml dimethyl acetamide (DMA) was heated to 373 K in a sealed 10 ml Teflon-lined reactor for 72 h. The mixture was allowed to cool to room temperature and the resulting block-shaped colorless crystals filtered from the reaction mixture. Yield, 72%.

S3. Refinement

The H atoms on water were located in a difference Fourier map and refined in riding mode with the fixed U_{iso}(H) = 0.105 Å^2. The aromatic H atoms were placed at calculated positions and were treated as riding on the parent C atoms with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C).
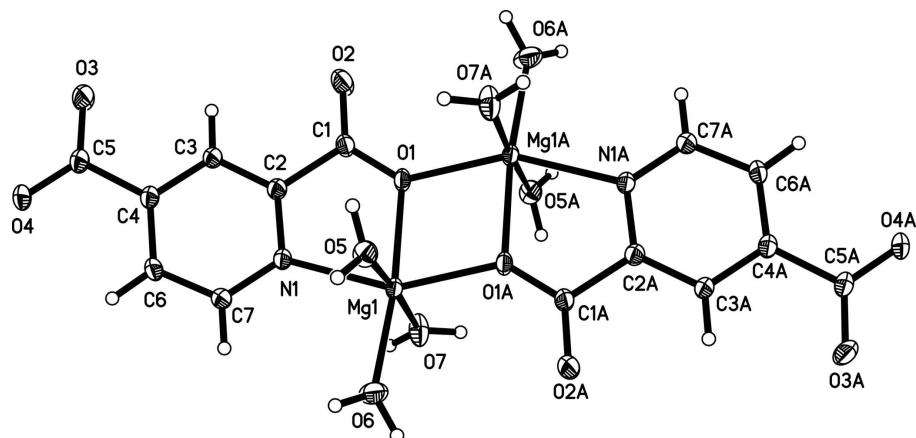
Figure 1

The molecular structure of the title compound, showing 30% probability displacement ellipsoids.
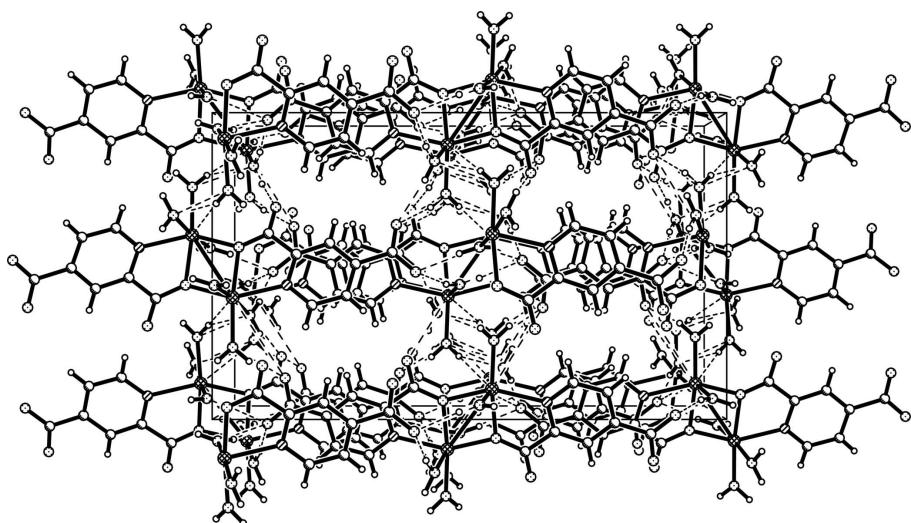
Figure 2

The packing diagram of the title complex.

Bis(μ-pyridine-2,4-dicarboxylato)- κ³N,O²:O²;κ³O²:N,O²- bis[triaquamagnesium(II)]

Crystal data

$[Mg_2(C_7H_3NO_4)_2(H_2O)_6]$	$F(000) = 1008$
$M_r = 486.92$	$D_x = 1.663$ Mg m^{-3}
Orthorhombic, *Pbca*	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ac 2ab	Cell parameters from 2705 reflections
$a = 7.9221$ (8) Å	$\theta = 3.2–26.8°$
$b = 12.0951$ (12) Å	$\mu = 0.21$ mm^{-1}
$c = 20.2989$ (18) Å	$T = 293$ K
$V = 1945.0$ (3) Å^3	Block, colorless
$Z = 4$	$0.25 \times 0.18 \times 0.15$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	8884 measured reflections
Radiation source: fine-focus sealed tube	1719 independent reflections
Graphite monochromator	1289 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.042$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 25.0°$, $\theta_{min} = 2.0°$
	$h = -5 \rightarrow 9$
$T_{min} = 0.951$, $T_{max} = 0.970$	$k = -14 \rightarrow 14$
	$l = -24 \rightarrow 23$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.040$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.100$	
$S = 1.06$	H-atom parameters constrained
1719 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 1.7679P]$ where $P = (F_o^2 + 2F_c^2)/3$
145 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.36$ e Å^{-3}
	$\Delta\rho_{min} = -0.30$ e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mg1	0.07954 (11)	0.60169 (7)	0.04323 (3)	0.0240 (2)
O1	−0.0075 (2)	0.43818 (14)	0.05141 (7)	0.0272 (4)
O2	−0.0923 (4)	0.30663 (19)	0.12021 (10)	0.0760 (9)
O3	−0.0102 (4)	0.3649 (2)	0.35781 (9)	0.0875 (11)
H6A	0.1178	0.8068	0.0765	0.105*
H5B	−0.1892	0.7246	0.0848	0.105*
H5A	−0.2377	0.6193	0.0826	0.105*
H7A	0.3503	0.5401	−0.0194	0.105*
H7B	0.4054	0.5600	0.0457	0.105*
H6B	0.2174	0.8016	0.0211	0.105*
O4	0.1026 (2)	0.51899 (15)	0.39638 (8)	0.0364 (5)
O5	−0.1604 (2)	0.66298 (14)	0.06670 (8)	0.0323 (5)
O6	0.1539 (3)	0.76106 (16)	0.04659 (9)	0.0491 (6)
O7	0.3209 (2)	0.56088 (17)	0.01937 (8)	0.0430 (5)
N1	0.1126 (3)	0.56101 (17)	0.14911 (9)	0.0257 (5)
C1	−0.0232 (4)	0.3941 (2)	0.10852 (11)	0.0325 (6)

C2	0.0461 (3)	0.4620 (2)	0.16485 (11)	0.0261 (6)
C3	0.0314 (3)	0.4258 (2)	0.22895 (11)	0.0302 (6)
H3	−0.0135	0.3564	0.2378	0.036*
C4	0.0838 (3)	0.4934 (2)	0.28011 (11)	0.0281 (6)
C5	0.0576 (4)	0.4556 (2)	0.35037 (12)	0.0361 (7)
C6	0.1530 (4)	0.5952 (2)	0.26430 (11)	0.0318 (6)
H6	0.1902	0.6426	0.2973	0.038*
C7	0.1660 (4)	0.6255 (2)	0.19836 (11)	0.0325 (6)
H7	0.2139	0.6935	0.1881	0.039*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0328 (5)	0.0234 (5)	0.0157 (4)	−0.0004 (4)	0.0015 (3)	−0.0008 (3)
O1	0.0415 (11)	0.0250 (10)	0.0151 (8)	0.0001 (8)	−0.0028 (8)	0.0000 (7)
O2	0.151 (3)	0.0485 (15)	0.0289 (11)	−0.0543 (16)	−0.0205 (13)	0.0080 (10)
O3	0.176 (3)	0.0627 (17)	0.0241 (11)	−0.0682 (19)	0.0088 (14)	0.0028 (10)
O4	0.0497 (12)	0.0419 (12)	0.0176 (8)	−0.0064 (9)	−0.0043 (8)	−0.0016 (8)
O5	0.0379 (11)	0.0271 (10)	0.0320 (9)	0.0057 (8)	0.0049 (8)	−0.0031 (8)
O6	0.0683 (15)	0.0308 (11)	0.0482 (12)	−0.0158 (10)	0.0282 (11)	−0.0089 (9)
O7	0.0339 (11)	0.0693 (15)	0.0260 (9)	0.0104 (10)	−0.0014 (8)	−0.0103 (9)
N1	0.0348 (13)	0.0239 (12)	0.0185 (10)	−0.0021 (9)	−0.0003 (9)	0.0002 (8)
C1	0.0538 (18)	0.0229 (14)	0.0208 (13)	−0.0060 (13)	−0.0040 (12)	−0.0003 (11)
C2	0.0327 (15)	0.0238 (14)	0.0220 (12)	−0.0006 (11)	−0.0008 (11)	0.0010 (10)
C3	0.0445 (17)	0.0256 (14)	0.0205 (12)	−0.0074 (12)	−0.0023 (12)	0.0028 (10)
C4	0.0349 (15)	0.0301 (15)	0.0194 (12)	−0.0011 (12)	−0.0010 (11)	0.0007 (10)
C5	0.0526 (19)	0.0362 (17)	0.0193 (13)	−0.0074 (14)	−0.0014 (12)	0.0027 (12)
C6	0.0449 (16)	0.0308 (15)	0.0196 (12)	−0.0068 (13)	−0.0052 (12)	−0.0026 (10)
C7	0.0466 (17)	0.0275 (15)	0.0236 (13)	−0.0102 (13)	−0.0025 (12)	0.0009 (11)

Geometric parameters (Å, º)

Mg1—N1	2.2202 (19)	O7—H7A	0.8581
Mg1—O1	2.1011 (19)	O7—H7B	0.8563
Mg1—O1^i	2.0613 (16)	N1—C7	1.336 (3)
Mg1—O5	2.0953 (19)	N1—C2	1.347 (3)
Mg1—O6	2.017 (2)	C1—C2	1.511 (3)
Mg1—O7	2.033 (2)	C2—C3	1.378 (3)
O1—C1	1.282 (3)	C3—C4	1.385 (3)
O2—C1	1.215 (3)	C3—H3	0.9300
O3—C5	1.231 (3)	C4—C6	1.385 (4)
O4—C5	1.260 (3)	C4—C5	1.512 (3)
O5—H5B	0.8616	C6—C7	1.392 (3)
O5—H5A	0.8701	C6—H6	0.9300
O6—H6A	0.8688	C7—H7	0.9300
O6—H6B	0.8725		
O6—Mg1—O7	88.02 (9)	H6A—O6—H6B	104.2

O6—Mg1—O1^i	109.63 (8)	Mg1—O7—H7A	123.0
O7—Mg1—O1^i	88.93 (7)	Mg1—O7—H7B	126.1
O6—Mg1—O5	85.36 (8)	H7A—O7—H7B	110.8
O7—Mg1—O5	173.33 (9)	C7—N1—C2	117.7 (2)
O1^i—Mg1—O5	92.50 (7)	C7—N1—Mg1	129.22 (17)
O6—Mg1—O1	173.16 (8)	C2—N1—Mg1	112.37 (15)
O7—Mg1—O1	95.68 (8)	O2—C1—O1	125.6 (2)
O1^i—Mg1—O1	76.26 (7)	O2—C1—C2	119.3 (2)
O5—Mg1—O1	90.98 (8)	O1—C1—C2	115.0 (2)
O6—Mg1—N1	98.32 (8)	N1—C2—C3	122.7 (2)
O7—Mg1—N1	93.77 (8)	N1—C2—C1	116.5 (2)
O1^i—Mg1—N1	152.00 (8)	C3—C2—C1	120.7 (2)
O5—Mg1—N1	88.02 (8)	C2—C3—C4	119.7 (2)
O1—Mg1—N1	75.74 (7)	C2—C3—H3	120.2
O6—Mg1—Mg1^i	148.06 (7)	C4—C3—H3	120.2
O7—Mg1—Mg1^i	92.97 (6)	C6—C4—C3	118.0 (2)
O1^i—Mg1—Mg1^i	38.56 (5)	C6—C4—C5	122.8 (2)
O5—Mg1—Mg1^i	92.20 (6)	C3—C4—C5	119.2 (2)
O1—Mg1—Mg1^i	37.70 (4)	O3—C5—O4	125.1 (2)
N1—Mg1—Mg1^i	113.44 (7)	O3—C5—C4	116.5 (2)
C1—O1—Mg1^i	135.94 (16)	O4—C5—C4	118.4 (2)
C1—O1—Mg1	119.66 (15)	C4—C6—C7	119.1 (2)
Mg1^i—O1—Mg1	103.74 (7)	C4—C6—H6	120.5
Mg1—O5—H5B	130.0	C7—C6—H6	120.5
Mg1—O5—H5A	120.5	N1—C7—C6	122.9 (2)
H5B—O5—H5A	100.5	N1—C7—H7	118.6
Mg1—O6—H6A	122.4	C6—C7—H7	118.6
Mg1—O6—H6B	133.3		

Symmetry code: (i) −x, −y+1, −z.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···O4^{ii}	0.87	1.80	2.668 (3)	172
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O7—H7B···O4^{vii}	0.86	2.02	2.857 (3)	166

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