

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Tetraaqua(2,2'-bipyridine- κ^2N,N')-magnesium(II) bis(4-fluorobenzoate)

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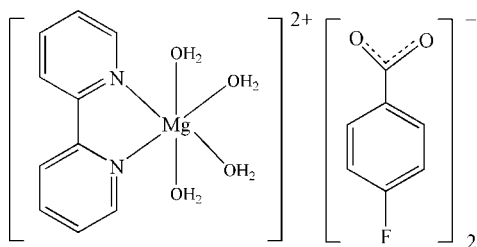
Received 4 November 2010; accepted 17 November 2010

Key indicators: single-crystal X-ray study; $T = 290$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.070; wR factor = 0.207; data-to-parameter ratio = 14.8.

The title compound, $[\text{Mg}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4](\text{C}_7\text{H}_4\text{FO}_2)_2$, consists of a bivalent $[\text{Mg}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4]^{2+}$ cation and two 4-fluorobenzoate anions. In the complex cation, the Mg^{II} atom is coordinated by two N atoms from a 2,2'-bipyridine ligand and four water O atoms in a distorted MgN_2O_4 octahedral geometry. The Mg^{II} atom is located on a twofold rotation axis and thus a cation exhibits C_2 molecular symmetry. The 2,2'-bipyridine ligands exhibit nearly perfect planarity (r.m.s. deviations = 0.0061 Å). In the crystal, $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds link the cations and anions into a three-dimensional supramolecular network.

Related literature

For related magnesium(II) complexes with 1,10-phenanthroline and pyridine ligands, see: Halut-Desportes (1981); Hao *et al.* (2008); Zhang (2004); Zhang *et al.* (2010).



Experimental

Crystal data

 $[\text{Mg}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4](\text{C}_7\text{H}_4\text{FO}_2)_2$ $M_r = 530.76$
Orthorhombic, $Pbcn$
 $a = 27.911$ (6) Å
 $b = 12.423$ (3) Å
 $c = 7.5895$ (15) Å
 $V = 2631.6$ (10) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.13$ mm⁻¹
 $T = 290$ K
 $0.18 \times 0.13 \times 0.10$ mm

Data collection

 Rigaku R-AXIS RAPID
 diffractometer
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
 $T_{\text{min}} = 0.979$, $T_{\text{max}} = 0.987$

 2316 measured reflections
 2310 independent reflections
 1741 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.096$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.070$
 $wR(F^2) = 0.207$
 $S = 1.14$
 2310 reflections

 156 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1A}\cdots\text{O4}^{\text{ii}}$	0.82	1.90	2.715 (4)	172
$\text{O1}-\text{H1B}\cdots\text{O4}^{\text{ii}}$	0.82	1.90	2.682 (4)	159
$\text{O2}-\text{H2A}\cdots\text{O3}^{\text{iii}}$	0.82	1.84	2.661 (3)	173
$\text{O2}-\text{H2B}\cdots\text{O4}^{\text{ii}}$	0.82	1.99	2.796 (5)	167
$\text{C3}-\text{H3}\cdots\text{O3}^{\text{iv}}$	0.93	2.55	3.257 (6)	133

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); 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: *SHELXL97*.

The authors gratefully acknowledge financial support by the Education Office of Zhejiang Province (grant No. 20051316) and the Scientific Research Fund of Ningbo University (grant No. XKL09078).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2287).

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supporting information

Acta Cryst. (2010). E66, m1624 [https://doi.org/10.1107/S1600536810047690]

Tetraaqua(2,2'-bipyridine- κ^2 N,N')magnesium(II) bis(4-fluorobenzoate)**Bi-Song Zhang, Jian-Ping Qiu, Li-Hua Liu and Wei Xu****S1. Comment**

Magnesium(II) ions with 1.10-phenanthroline(phen) and pyridine(bipy) ligands can form tetraaqua(L)_nMagnesium(II)(L = phen, n = 1; L = bipy, n = 2) complex cation (Halut-Desportes, 1981, Hao, *et al.*, 2008, Zhang, 2004, Zhang, *et al.*,2010.) In this paper we report synthesis and structure of the title compound. The crystal structure of title compound consists of [Mg(H₂O)₄(2,2'-bpy)]²⁺ complex cations and 4-fluorbenzoate anion (Fig. 1). the cation placed in special position on twofold axis which passes through Mg^{II} atom and middle C5—C5' bond of 2,2'-bipy molecule; Symmetry code:(i)-x,y,-z+1/2. In the cation, the Mg^{II} atom is coordinated by two N atoms from one 2,2'-bipy ligands, four O atoms from four different water molecules, completing a distorted MgN₂O₄ octahedral geometry. The Mg—N bond length is 2.183 (3) Å and Mg—O bond lengths are 2.040 (2) and 2.061 (2)Å. The chelating bipy ligands exhibit nearly perfect planarity (r.m.s. deviations = 0.0061 Å). The mean interplanar distances of 3.8352 (3) Å between adjacent bipy ligands indicate π - π stacking interactions (very weak). The complex cations and 4-fluorbenzoate anions are connected via O—H \cdots O and C—H \cdots O hydrogen bonds (Table 1, Fig. 2) into a three-dimensional supramolecular network.

S2. Experimental

[Mg(OH)₂.4MgCO₃.4H₂O] (0.4900 g, 1.00 mmol), 4-fluorbenzoate acid (0.0602 g, 0.43 mmol),2,2'-bipyridine (bipy) (0.0503 g, 0.32 mmol), CH₃OH/H₂O (v/v = 1:2, 15 mL) were mixed and stirred for 2.0 h. Subsequently, the resulting cream suspension was heated in a 23 mL Teflon-lined stainless steel autoclave at 453 K for 5800 minutes. After the autoclave was cooled to room temperature according to the procedure for 2600 minutes, the solid was filtered off. The resulting filtrate was allowed to stand at room temperature, and slow evaporation for 2 months afforded colourless block single crystals.

S3. Refinement

C-bound H atoms were placed in calculated positions, with C—H = 0.93Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and were refined using the riding- model approximation. The H atoms of the water molecule were located in a difference Fourier map and refined with an O—H distance restraint of 0.82 (1) Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

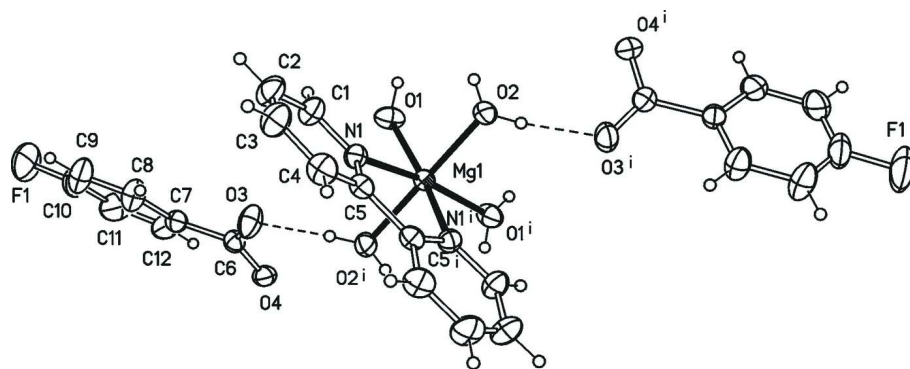


Figure 1

The molecule structure of the title compound showing the atom-labelling scheme. The octahedral $[\text{Mg}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4]^{2+}$ complex cation is balanced by two fluorbenzoate anions. The two coordinated water molecules of the complex cation are hydrogen bonded to two anions. Displacement ellipsoids are drawn at the 40% probability level (symmetry code:(i)-x,y,-z+1/2).

Data collection

Rigaku R-AXIS RAPID
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 ω scans
Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)
 $T_{\min} = 0.979$, $T_{\max} = 0.987$

2316 measured reflections
2310 independent reflections
1741 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.096$
 $\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 3.2^\circ$
 $h = -33 \rightarrow 33$
 $k = -14 \rightarrow 14$
 $l = -8 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.070$
 $wR(F^2) = 0.207$
 $S = 1.14$
2310 reflections
156 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
 $w = 1/[\sigma^2(F_o^2) + (0.0879P)^2 + 2.3043P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Mg1	0.0000	0.29487 (11)	0.2500	0.0347 (4)
O1	0.05496 (9)	0.4005 (2)	0.2115 (3)	0.0536 (7)
H1A	0.0576	0.4581	0.2632	0.080*
H1B	0.0657	0.4124	0.1128	0.080*
O2	-0.01046 (8)	0.2966 (2)	-0.0187 (3)	0.0509 (7)
H2A	-0.0378	0.2905	-0.0568	0.076*
H2B	0.0122	0.3254	-0.0688	0.076*
O3	0.40257 (9)	0.2093 (2)	0.1617 (4)	0.0680 (9)
O4	0.42874 (8)	0.0949 (2)	0.3633 (3)	0.0482 (7)
N1	0.04711 (9)	0.1555 (2)	0.2250 (4)	0.0418 (7)
F1	0.20665 (10)	0.0891 (3)	0.5077 (5)	0.1243 (14)
C1	0.09402 (13)	0.1603 (3)	0.1902 (5)	0.0544 (10)
H1	0.1090	0.2271	0.1896	0.065*
C2	0.12112 (15)	0.0689 (4)	0.1551 (6)	0.0682 (12)
H2	0.1537	0.0746	0.1312	0.082*
C3	0.09930 (15)	-0.0285 (4)	0.1561 (6)	0.0689 (12)

H3	0.1167	-0.0906	0.1313	0.083*
C4	0.05129 (15)	-0.0346 (3)	0.1944 (6)	0.0586 (10)
H4	0.0360	-0.1011	0.1969	0.070*
C5	0.02579 (12)	0.0585 (3)	0.2293 (4)	0.0415 (8)
C6	0.39599 (12)	0.1476 (3)	0.2874 (5)	0.0426 (8)
C7	0.34578 (6)	0.1330 (2)	0.3515 (3)	0.0454 (8)
C8	0.31097 (9)	0.20812 (19)	0.3063 (4)	0.0666 (12)
H8	0.3192	0.2683	0.2400	0.080*
C9	0.26384 (8)	0.1933 (2)	0.3604 (5)	0.0860 (16)
H9	0.2405	0.2436	0.3302	0.103*
C10	0.25153 (7)	0.1034 (3)	0.4595 (4)	0.0789 (14)
C11	0.28634 (10)	0.0283 (2)	0.5047 (4)	0.0844 (17)
H11	0.2781	-0.0319	0.5710	0.101*
C12	0.33346 (9)	0.0431 (2)	0.4506 (4)	0.0663 (12)
H12	0.3568	-0.0072	0.4808	0.080*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0374 (8)	0.0321 (8)	0.0346 (8)	0.000	-0.0008 (6)	0.000
O1	0.0681 (16)	0.0475 (14)	0.0450 (13)	-0.0212 (12)	0.0090 (12)	-0.0062 (12)
O2	0.0452 (14)	0.0697 (17)	0.0379 (13)	-0.0083 (12)	-0.0036 (10)	0.0040 (12)
O3	0.0505 (16)	0.076 (2)	0.0771 (19)	0.0115 (13)	0.0175 (14)	0.0332 (16)
O4	0.0473 (14)	0.0502 (15)	0.0472 (13)	0.0034 (11)	-0.0090 (11)	-0.0031 (11)
N1	0.0400 (16)	0.0406 (16)	0.0448 (15)	0.0030 (12)	-0.0008 (12)	-0.0011 (13)
F1	0.0611 (18)	0.169 (4)	0.143 (3)	-0.0280 (19)	0.0441 (18)	-0.016 (3)
C1	0.043 (2)	0.049 (2)	0.071 (3)	0.0030 (16)	0.0017 (18)	-0.0011 (19)
C2	0.047 (2)	0.072 (3)	0.085 (3)	0.015 (2)	0.010 (2)	-0.003 (2)
C3	0.066 (3)	0.052 (3)	0.089 (3)	0.024 (2)	0.006 (2)	-0.008 (2)
C4	0.070 (3)	0.036 (2)	0.070 (2)	0.0086 (18)	0.001 (2)	-0.0039 (18)
C5	0.0502 (19)	0.0371 (18)	0.0372 (17)	0.0012 (15)	-0.0021 (15)	-0.0001 (14)
C6	0.0430 (19)	0.0397 (19)	0.0451 (19)	0.0027 (15)	0.0018 (15)	-0.0051 (16)
C7	0.0430 (19)	0.050 (2)	0.0434 (18)	-0.0033 (16)	0.0019 (15)	-0.0017 (16)
C8	0.051 (2)	0.057 (2)	0.092 (3)	0.0051 (19)	0.013 (2)	0.007 (2)
C9	0.050 (3)	0.086 (4)	0.122 (4)	0.011 (2)	0.016 (3)	-0.004 (3)
C10	0.054 (3)	0.104 (4)	0.079 (3)	-0.017 (3)	0.023 (2)	-0.010 (3)
C11	0.073 (3)	0.112 (5)	0.068 (3)	-0.035 (3)	0.005 (2)	0.027 (3)
C12	0.059 (2)	0.081 (3)	0.059 (2)	-0.013 (2)	-0.0045 (19)	0.020 (2)

Geometric parameters (Å, °)

Mg1—O1 ⁱ	2.040 (2)	C2—H2	0.9300
Mg1—O1	2.040 (2)	C3—C4	1.373 (6)
Mg1—O2	2.061 (2)	C3—H3	0.9300
Mg1—O2 ⁱ	2.061 (2)	C4—C5	1.384 (5)
Mg1—N1 ⁱ	2.183 (3)	C4—H4	0.9300
Mg1—N1	2.183 (3)	C5—C5 ⁱ	1.473 (7)
O1—H1A	0.8200	C6—C7	1.494 (4)

O1—H1B	0.8200	C7—C8	1.3900
O2—H2A	0.8201	C7—C12	1.3900
O2—H2B	0.8198	C8—C9	1.3900
O3—C6	1.238 (4)	C8—H8	0.9300
O4—C6	1.263 (4)	C9—C10	1.3900
N1—C1	1.337 (4)	C9—H9	0.9300
N1—C5	1.344 (4)	C10—C11	1.3900
F1—C10	1.317 (3)	C11—C12	1.3900
C1—C2	1.390 (6)	C11—H11	0.9300
C1—H1	0.9300	C12—H12	0.9300
C2—C3	1.355 (6)		
O1 ⁱ —Mg1—O1	99.93 (16)	C2—C3—C4	119.3 (4)
O1 ⁱ —Mg1—O2	91.62 (10)	C2—C3—H3	120.4
O1—Mg1—O2	87.60 (10)	C4—C3—H3	120.4
O1 ⁱ —Mg1—O2 ⁱ	87.60 (10)	C3—C4—C5	119.8 (4)
O1—Mg1—O2 ⁱ	91.62 (10)	C3—C4—H4	120.1
O2—Mg1—O2 ⁱ	178.78 (17)	C5—C4—H4	120.1
O1 ⁱ —Mg1—N1 ⁱ	92.57 (11)	N1—C5—C4	121.1 (3)
O1—Mg1—N1 ⁱ	167.41 (12)	N1—C5—C5 ⁱ	115.97 (18)
O2—Mg1—N1 ⁱ	90.53 (10)	C4—C5—C5 ⁱ	122.9 (2)
O2 ⁱ —Mg1—N1 ⁱ	90.44 (11)	O3—C6—O4	124.4 (3)
O1 ⁱ —Mg1—N1	167.41 (12)	O3—C6—C7	117.7 (3)
O1—Mg1—N1	92.57 (11)	O4—C6—C7	117.9 (3)
O2—Mg1—N1	90.44 (11)	C8—C7—C12	120.0
O2 ⁱ —Mg1—N1	90.53 (10)	C8—C7—C6	119.6 (2)
N1 ⁱ —Mg1—N1	74.99 (15)	C12—C7—C6	120.4 (2)
Mg1—O1—H1A	124.2	C7—C8—C9	120.0
Mg1—O1—H1B	121.4	C7—C8—H8	120.0
H1A—O1—H1B	104.3	C9—C8—H8	120.0
Mg1—O2—H2A	118.7	C8—C9—C10	120.0
Mg1—O2—H2B	110.7	C8—C9—H9	120.0
H2A—O2—H2B	126.6	C10—C9—H9	120.0
C1—N1—C5	118.6 (3)	F1—C10—C11	120.4 (3)
C1—N1—Mg1	124.9 (2)	F1—C10—C9	119.6 (3)
C5—N1—Mg1	116.2 (2)	C11—C10—C9	120.0
N1—C1—C2	122.3 (4)	C10—C11—C12	120.0
N1—C1—H1	118.8	C10—C11—H11	120.0
C2—C1—H1	118.8	C12—C11—H11	120.0
C3—C2—C1	118.9 (4)	C11—C12—C7	120.0
C3—C2—H2	120.5	C11—C12—H12	120.0
C1—C2—H2	120.5	C7—C12—H12	120.0

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A \cdots O4 ⁱⁱ	0.82	1.90	2.715 (4)	172

O1—H1B···O4 ⁱⁱⁱ	0.82	1.90	2.682 (4)	159
O2—H2A···O3 ^{iv}	0.82	1.84	2.661 (3)	173
O2—H2B···O4 ⁱⁱⁱ	0.82	1.99	2.796 (5)	167
C3—H3···O3 ^v	0.93	2.55	3.257 (6)	133

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