



Research Article

ISSN : 0975-7384  
CODEN(USA) : JCPRC5

## Synthesis and crystal structure of Mg (II) complex with 3-amino-2-pyrazinecarboxylic acid ligand

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### ABSTRACT

A novel complex,  $[Mg(L)_2(H_2O)_2] \cdot (H_2O)$  [ $L = 3\text{-amino-2-pyrazinecarboxylic acid}$ ] was synthesized in ethanol/ $H_2O$  ( $v:v=3:1$ ) with magnesium chloride hexahydrate and 3-amino-2-pyrazinecarboxylic acid as raw materials. It was characterized by elemental analysis, IR and X-ray single crystal diffraction analysis. The crystal of the title complex  $[Mg(L)_2(H_2O)_2] \cdot (H_2O)$  belongs to orthorhombic, space group  $P-1$  with  $a = 2.9288(6)$  nm,  $b = 0.82286(16)$  nm,  $c = 1.2132(2)$  nm,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 2.9238(10)$  nm<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.611$   $\mu\text{g}\cdot\text{m}^{-3}$ ,  $\mu = 0.173$  mm<sup>-1</sup>,  $F(000) = 1472$ , and final  $R_1 = 0.0247$ ,  $wR_2 = 0.0697$ . X-ray analysis reveals that the complex comprises a six-coordinated magnesium (II) center, with a  $N_2O_4$  distorted octahedron coordination environment. The molecules are connected by hydrogen bonds and  $\pi$ - $\pi$  stacking to form one dimensional chain structure.

**Key words:** 3-Amino-2-pyrazinecarboxylic acid; Mg (II) complex; synthesis; crystal structure

### INTRODUCTION

Over the past decade, the design and synthesis of metal complex materials have attracted intense attention due to their potential practical applications, such as molecule-based magnets, luminescence, antimicrobial agents and antitumor activities [1-7]. Increasing investigations have been focused on the transition metal complex materials [8-15]. Magnesium is an indispensable element in biology. It is involved in several biochemical processes and is an essential cofactor required for the activation of a variety of enzymes. So it is significance to study on the structure and characteristic coordination of magnesium carefully for making sure about physiological and biochemical mechanisms of all lives. To the best of our knowledge, the magnesium (II) complex materials with carboxylate ligands have been much less extensively studied than other metal complexes. In this paper, we report the synthesis and X-ray crystal structure of  $[Mg(L)_2(H_2O)_2] \cdot (H_2O)$ .

### EXPERIMENTAL SECTION

The following A. R. grade chemicals were used for the preparation of the studied compound without further purifications: magnesium chloride hexahydrate, 3-amino-2-pyrazinecarboxylic acid, sodium hydroxide. The carbon, hydrogen and nitrogen content in the newly synthesized complex were determined on a Elementar Vario III EL elemental analyzer. Infrared spectrum (4000-400 cm<sup>-1</sup>) was recorded with KBr optics on a Nicolet AVATAR 360 FTIR spectrophotometer. The crystal data was collected on a Bruker smart CCD Area Detector.

#### Synthesis of the Mg(II) complex

A solution of 3-amino-2-pyrazinecarboxylic acid (1.0 mmol, 0.139 g) and sodium hydroxide (1.0 mmol 0.04 g) in 10 mL  $\text{CH}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$  ( $v:v=3:1$ ) was stirred at 60 °C. Then 0.5 mmol (0.1015 g) of magnesium chloride hexahydrate was added to the above solution. The mixture was continuously stirred for 4 h at refluxing temperature. The mixture

was cooled at room temperature, and the resulting solution was filtered. The colourless crystals were obtained after the filtrate was kept in air for 2 weeks. Yield: 58%. Elementary analysis: calcd for  $C_{10}H_{14}MgN_6O_7$ : C, 33.84; H, 3.95; N, 23.69 %; found: C, 33.58; H, 3.69; N, 23.72 %. IR  $\nu_{max}$  ( $cm^{-1}$ ):  $\nu_{as}(COO^-)$ : 1692  $cm^{-1}$ ,  $\nu_s(COO^-)$ : 1547  $cm^{-1}$ ,  $\nu(NH_2)$ : 2926  $cm^{-1}$ ,  $\nu(H_2O)$ : 3328  $cm^{-1}$ ,  $\nu(Mg-O)$ : 427  $cm^{-1}$ .

### X-ray Crystallography

A colourless block single crystal with dimensions of 0.28 mm×0.24 mm×0.20 mm was selected for measurement. Diffraction data of the single crystal were collected by  $\varphi\sim\omega$  scan mode using a graphite-monochromatic Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293 (2) K on a Bruker Smart Apex CCD diffractometer. A total of 4494 reflections were collected in the range 2.78-28.31°, of which 1636 were unique ( $R_{int} = 0.0191$ ) and 1594 were observed with  $I > 2\sigma(I)$ . The data were corrected for  $Lp$  factors. The structure was solved by direct methods and refined by full-matrix least-squares techniques on  $F^2$ . The structure was solved by direct methods [16] using SHELXL-97 and expanded using Fourier techniques. All of the non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. The final refinement by full-matrix least squares method was converged at  $R = 0.0247$ , and  $wR = 0.0697$  ( $w = 1/[\delta^2(Fo^2) + (0.0504P)^2 + 0.3132P]$ ,  $P = (Fo^2 + 2Fc^2)/3$ ,  $S = 1.075$ ,  $(\Delta/\sigma)_{max} = 0.001$ ). The largest peak in the final difference fourier map is 0.163 e /  $\text{\AA}^3$  and the minimum peak is -0.175 e /  $\text{\AA}^3$ . Molecular graphics were drawn with the program package SHELXTL-97 crystallographic software package [17]. The most relevant crystal data for complex are quoted in Table 1, and the selected bond distances and angles are listed in Table 2.

Table 1: Crystallographic data for Mg (II) complex

Formula	$C_{10}H_{14}MgN_6O_7$
Formula weight	354.58
Crystal system	Orthorhombic
Space group	$P-1$
a ( $\text{\AA}$ )	29.288(6)
b ( $\text{\AA}$ )	8.2286(16)
c ( $\text{\AA}$ )	12.132(2)
$\alpha = \beta = \gamma$ ( $^\circ$ )	90
Z	8
$F(000)$	1472
Temperature (K)	293(2)
V ( $\text{\AA}^3$ )	2923.8(10)
Calculated density ( $\mu g \cdot m^{-3}$ )	1.611
Crystal size ( $mm^3$ )	0.28×0.24×0.20
$\mu$ ( $mm^{-1}$ )	0.173
S	1.075
Limiting indices	$-9 \leq h \leq 9$ , $-18 \leq k \leq 16$ , $-18 \leq l \leq 18$
Reflections collected / unique	4494/1594
$R_1, wR_2$ [all data]	0.0254, 0.0703
$R_1, wR_2$ [ $I > 2\sigma(I)$ ]	0.0247, 0.0697
Largest diff. peak and hole ( $e \cdot \text{\AA}^{-3}$ )	0.163, -0.175

Table 2: Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for Mg (II) complex

Bond	Distance	Bond	Distance
Mg1-O3	2.0304(11)	C5-O2	1.2472(16)
Mg1-O3A	2.0304(11)	N3-C4	1.3189(15)
Mg1-O2A	2.0470(11)	C1-N3	1.3275(16)
Mg1-O2	2.0470(11)	N2-C2	1.314(2)
Mg1-N3A	2.2091(11)	N2-C3	1.3353(18)
Mg1-N3	2.2091(11)		
Angle ( $^\circ$ )		Angle ( $^\circ$ )	
O3-Mg1-O3A	89.90(7)	O3-Mg1-N3	96.28(4)
O3-Mg1-O2A	167.55(4)	O3A-Mg1-N3	91.82(4)
O3A-Mg1-O2A	89.28(5)	N3-Mg1-O2A	96.16(4)
O2-Mg1-O3	89.28(5)	O2-Mg1-N3	75.93(4)
O2-Mg1-O3A	167.55(4)	N3A-Mg1-N3	168.56(6)
O2A-Mg1-O2	94.16(7)	O1-C5-O2	125.28(12)
O3-Mg1-N3A	91.82(4)	O1-C5-C4	118.03(11)
O3A-Mg1-N3A	96.28(4)	O2-C5-C4	116.68(11)
O2A-Mg1-N3A	75.93(4)	C1-N3-C4	119.03(10)
O2-Mg1-N3A	96.16(4)	C3-N2-C2	117.76(12)

Symmetry code:  $-x+1, -y, z$

## RESULTS AND DISCUSSION

The results of elemental analysis indicated that the composition of the Mg (II) complex conforms to  $[\text{Mg}(\text{L})_2(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})$ , and that the complex conforms to a 1:2 metal-to-ligand stoichiometry. The solubility of Mg (II) complex was determined at room temperature, and the results showed that the Mg (II) complex is soluble in DMF, DMSO, methanol, methanol and  $\text{H}_2\text{O}$ , insoluble in benzene, diethyl ether and chloroform.

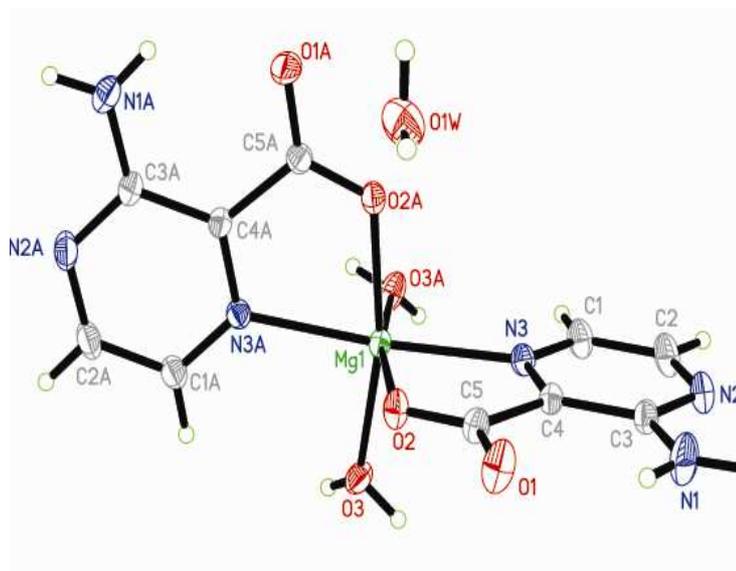
**Infrared spectra**

In the infrared spectra, the  $\nu_{\text{as}}(\text{COOH})$  and  $\nu_{\text{s}}(\text{COOH})$  vibrations of the free ligand are at 1715 and 1605  $\text{cm}^{-1}$ , respectively. For the complex, the vibration observed at 1692  $\text{cm}^{-1}$  was assigned as  $\nu_{\text{as}}(\text{COO}^-)$  and that at 1547  $\text{cm}^{-1}$  as  $\nu_{\text{s}}(\text{COO}^-)$ . It can be explained that the carboxylate oxygen atoms of 3-amino-2-pyrazinecarboxylic acid ligand take part in the coordination with magnesium atom [18]. The difference between the  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  band is 145  $\text{cm}^{-1}$ , indicating an unidentate carboxylate moiety. The  $\nu(\text{C}=\text{N})$  vibration of the free ligand is at 1560  $\text{cm}^{-1}$ , and it shifts to 1547  $\text{cm}^{-1}$  in the complex, indicating that the nitrogen atoms of the ligand take part in the coordination with magnesium atom. The band of the  $\text{NH}_2$  groups at 2926  $\text{cm}^{-1}$  shows that there are uncoordinated atoms of the groups, because compared with the free ligand the strong absorption bands are not shifted. The new band at 427  $\text{cm}^{-1}$  is assigned to the  $\nu(\text{Mg}-\text{O})$  vibration. In addition, the band at 3328  $\text{cm}^{-1}$  shows that the complex contains water molecules, which are accordance with the results of elemental analysis.

**Structure Description**

The crystal structure of the title complex is revealed in Fig. 1. The molecular packing arrangement is shown in Fig. 2. As shown in Fig. 1, in the crystal structure, the Mg (II) ion is six-coordinated by two oxygen atoms (O2, O2A) from the 3-amino-2-pyrazinecarboxylic acid ligand, two oxygen atoms (O3, O3A) from the coordinated water molecules and two nitrogen atoms (N3, N3A) from the 3-amino-2-pyrazinecarboxylic acid ligand, forming up a distorted octahedral coordination geometry. The coordination atoms with O2, O2A, O3 and O3A atoms are situated equatorial plane and N3, N3A atoms are situated axial place. The axial bond angle N3-Mg1-N3A (168.56(6)°) is consistent with that of the literature structure (165.5(2)°) [19, 20]. The distances of the Mg-O bonds are in the range of 2.0304(11) ~ 2.0470(11) Å, and that of Mg-N bonds are 2.2091(11) Å, respectively, which are similar to the Mg-O bond and Mg-N bond lengths reported previously [20]. The dihedral angles between two pyrazine rings are 89.6°. There are strong hydrogen bonds in the crystal structure (Table 3).

The complex forms one dimensional chain structure along by N-H...O and O-H...O hydrogen bonds and  $\pi$ - $\pi$  stacking (Fig. 3). Obviously, these hydrogen bonds and  $\pi$ - $\pi$  interactions increase the stability of the crystal structure, and play an important role in the formation of 3D network structure (Fig. 2).



Symmetry code:  $-x+1, -y, z$

Fig 1: Molecular structure of the Mg (II) complex, where the thermal ellipsoids were drawn at 30% possibility

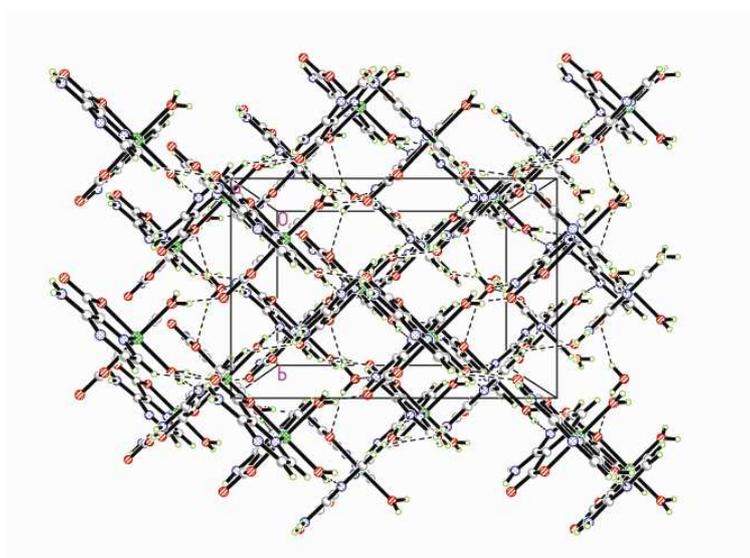
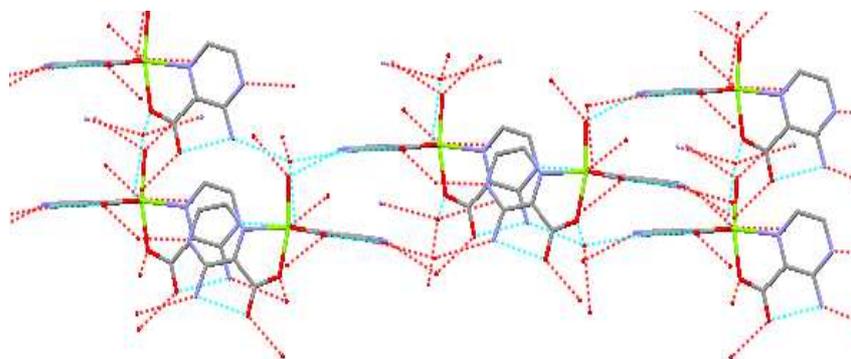


Fig 2: Packing of the Mg (II) complex

Fig 3: One dimensional chain structure of the Mg (II) complex by hydrogen bonds and  $\pi$ - $\pi$  stackingTable 3: Hydrogen bonds geometries ( $\text{\AA}$ ,  $^\circ$ )

D-H...A	D-H	H...A	D-A	$\angle$ DHA
O1W-H1A...O2	0.82	2.20	2.93	148
N1-H1A...O1W	0.86	2.18	3.03	168
N1-H1B...O1	0.86	2.05	2.68	130
O3-H3A...O1	0.81	1.88	2.68	167
O3-H3B...N2	0.85	1.95	2.79	165

## CONCLUSION

In summary, a novel complex  $[\text{Mg}(\text{L})_2(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})$  has been synthesized and structurally characterized. The results show that the ligand coordinated to the Mg (II) ion by nitrogen atoms and oxygen atoms and the complex molecule formed a distorted octahedron coordination environment. The molecules are connected by hydrogen bonds and  $\pi$ - $\pi$  stacking to form one dimensional chain structure.

### Supplementary Material

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 975303. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

### Acknowledgments

The authors would like to thank the National Natural Science Foundation of China (No. 21171132 and 20671073), the Promotive Research Fund for Excellent Young and Middle-aged Scientists' of Shandong Province (2010BSA07004) and Science Foundation of Weifang University.

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