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研究简报

二维氢键层状 Mg(Ⅱ)配合物的合成、晶体结构及其抗菌活性

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关键词: 2-羧基苯甲醛缩氨基硫脲; Mg(Ⅱ)配合物; 合成; 晶体结构; 抗菌活性

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Synthesis, Crystal Structure and Antibacterial Activity of 2D Hydrogen-bonds Layered Magnesium(Ⅱ) Complex

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Abstract: A new complex hexaaquamagnesium(Ⅱ) bis [2-(thiosemicarbazonomethyl)-benzoato], has been prepared and characterized by elemental analysis, IR spectra, molar conductivity and single-crystal X-ray diffraction. The results of crystal structure show that each Mg(Ⅱ) ion is coordinated with six oxygen atoms from water molecules and the complex formed two dimensional layered structure through intramolecule and intermolecule hydrogen bonds. The antibacterial assay of the magnesium(Ⅱ) complex and the ligand were tested using a modified version of the 2-fold serial dilution method, the results show that the complex show considerable antibacterial activity against *escherichia coli*, *bacillus subtilis* and *staphylococcus white*, and the ligand did not show antibacterial activity. CCDC: 751423.

Key words: 2-(thiosemicarbazonomethyl)-benzoato; magnesium complex; synthesis; crystal structure; antibacterial activity

Magnesium is indispensable element in biology. It is involved in several biochemical processes and is essential cofactor required for the activation of a variety of enzymes[1]. And it may increase the strength of cell membranes and regulate the function of the cell walls[2-3]. So magnesium plays an important role in the whole cell[4-8]. Moreover, it is the metal centre of the chlorophyll which can be photosynthetic, and is related to the mechanism of some drugs[9]. Thus, it is referred to the metal of life. 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[10].

Amino acid is an important physiological active substance. Besides bactericidal, insecticidal and anti-cancer biological activity, amino acids directly

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participate in biological processes, and are important to biochemistry and organic synthesis[11-14]. In this paper, a new magnesium complex of amino acid was synthesized, characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction. The complex formed two dimensional layered structure through intramolecule and intermolecule hydrogen bonds. The antibacterial activities of the magnesium (Ⅱ) complex and the ligand were tested.

1 Experimental

1.1 Materials and measurements

The following A.R. grade chemicals were used for the preparation of the studied compound: magnesium chloride, 2-carboxybenzaldehyde, thiosemicarbazide, sodium hydroxide.

The carbon, hydrogen and nitrogen content in the newly synthesized compound were analyzed on a Elementar Vario EL Ⅲ elemental analyzer. Infrared spectra (4 000~400 cm^{-1}) was determined with KBr optics on a Nicolet AVATAR 360 FTIR spectrophotometer. The molar conductance value was determined using a DDS-11A conductivity meter with CH_3OH as solvent (1 $mmol \cdot L^{-1}$ solution) at 25 ℃. The crystal data was collected on a Bruker Smart-1000 CCD Area Detector.

1.2 Synthesis of the ligand

10 mmol (1.501 3 g) of 2-carboxybenzaldehyde and 20 mmol (0.8 g) of sodium hydroxide were dissolved in 100 mL of water at room temperature, and added drop by drop 10 mmol (0.911 4 g) of thiosemicarbazide by stirring at room temperature. The reaction solution was kept running for 4 h, then acidified with the solution of hydrochloric acid (1∶1, *V*/*V*) to pH =2. The white solid precipitation were collected by filtration, washed and dried under vacuum. Yield may reach up to over 65%. Elemental analysis calculated for $C_9H_9N_3O_2S$(%): C 48.43, H 4.04, N 18.83; found(%): C 48.56, H 3.92, N 18.96. IR (KBr, cm^{-1}): 3 408br, 1 756s, 1 658s.

1.3 Synthesis of the complex

1.0 mmol (0.223 g) of 2-(thiosemicarbazonomethyl)-benzoic acid and 1.0 mmol (0.04 g) of sodium hydroxide were added to the 15 mL of CH_3OH/H_2O (2∶1, *V*/*V*) solution. After being dissolved, 0.5 mmol (0.102 g) of magnesium chloride was added to the solution. The mixture was continuously stirred for 3 h at refluxing temperature. The mixture was cooled at room temperature, and was collected by filtration. By evaporation in air at room temperature, the single crystal suitable for X-ray determination was obtained from methanol solution after 10 d. Yield 58%. Elemental analysis calculated for $C_{18}H_{28}MgN_6O_{10}S_2$(%): C 37.44, H 4.85, N 14.56; found(%): C 37.28, H 4.99, N 14.66. IR (KBr, cm^{-1}): 3 402br, 1 755s, 1 656s, 389m.

1.4 Antibacterial activity

The ligand and complex were dissolved in sterile water and tested against three reference strains for antibacterial activity, respectively. The antibacterial assay was performed using a modified version of the 2-fold serial dilution method[15], in which the concentration of chemical medicine decreased half as many in a sterile culture medium containing broth as the nutrient, and the strains were incubated 16 h in culture medium at constant temperature 37 ℃ after being activated, and misce bene after being added to the test tubes of chemical medicine, then readings were taken after 24 h of incubation at constant temperature 37 ℃. All other test conditions were standardized. The resultant turbidities in all tubes were estimated visually, and the lowest drug concentrations were found, which is defined MIC. After 48 h of continuous incubation, the MBC were defined, too.

1.5 Crystal structure determination

A colourless block single crystal with dimensions of 0.15 mm×0.12 mm×0.06 mm was placed on a glass fiber and mounted on a Bruker Smart-1000 CCD area detector. Diffraction data were collected by φ~ω scan mode using a graphite-monochromatic Mo $K\alpha$ radiation (λ=0.071 073 nm) at 273(2) K. A total of 6 596 reflections were collected in the range 1.58°~25.04°, of which 2 297 were unique (R_{int}=0.017 3) and 2 014 were observed with $I>2\sigma(I)$. The data were corrected for Lp factors. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques with SHELXL-97[17]. All non-

hydrogen atoms and hydr-ogen atoms were refined anisotropically and isotropi-cally, respectively. The final R=0.051 4, wR=0.128 0 (w=1/[$\sigma^2(F_o^2)$+(0.063 7P)^2], P =(F_o^2 +2F_c^2)/3 and S =1.226, $(\Delta/\sigma)_{max}$ =0.000). The largest peak in the final difference Fourier map is 902 e·nm^{-3} and the minimum peak is 433 e·nm^{-3}. Molecular graphics were drawn with the program package SHELXTL-97 crystallographic software package[18]. The most relevant crystal data for complex are quoted in Table 1.

CCDC: 751423

Table 1 Crystal structure parameters of the title complex

Formula	$C_{18}H_{28}MgN_6O_{10}S_2$	Temperature / K	273(2)
Formula weight	576.89	V / nm^3	1.325 7(3)
Crystal system	Monoclinic	Calculated density / (g·cm^{-3})	1.445
Space group	$P2_1/c$	Crystal size/ mm	0.15×0.12×0.06
a / nm	1.295 2(2)	θ range for data collection / (°)	1.58~25.04
b / nm	0.890 82(13)	Limiting indices	$-15\leqslant h\leqslant 15$, $-10\leqslant k\leqslant 10$, $-6\leqslant l\leqslant 13$
c / nm	1.153 65(17)	Reflections collected / unique	6 956 / 2 297
β / (°)	95.160(2)	R_1, wR_2 (all data)	0.057 8, 0.134 3
Z	2	R_1, wR_2 ($I>2\sigma(I)$)	0.051 4, 0.128 0
F(000)	604	Largest diff. peak and hole / (e·nm^{-3})	902 and −433

2 Results and discussion

2.1 Property of the complex

The results of elemental analyses and molar conductivity indicated that the composition of the complex as [Mg (H_2O)$_6$] (TCB)$_2$ (TCB =2-(thiosemicarbazonomethyl)-benzoato), indicating that the complex conforms to 1:2 (Mg/TCB) stoichiometry.

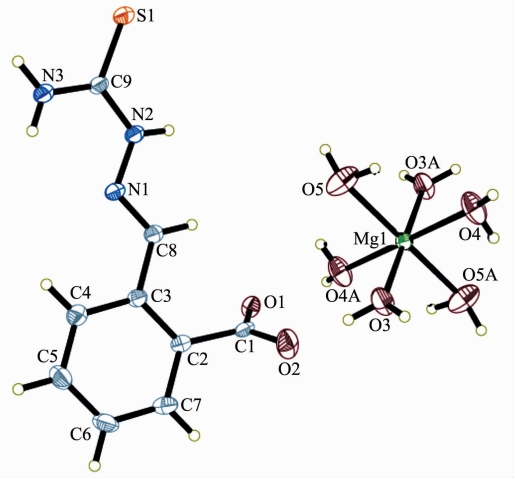
The complex is soluble in DMF, DMSO, methanol, a little soluble in ethanol and $CHCl_3$, insoluble in benzene, diethyl ether and cyclohexane. The molar conductance value of the complex measured in CH_3OH solution (1 mmol·L^{-1}) at 25 ℃ is 168 S·cm^2·mol^{-1}, indicating 1:2 electrolytes and that uncoordinated TCB are in the complex [19], which is in accordance with the results of IR spectra of the complex.

2.2 IR spectra

In the infrared spectra, the ν(COOH) vibrations of the free ligand are at 1 756 cm^{-1}. For the complex, the vibration observed at 1 755 cm^{-1} was assigned as ν_{as}(COO^-). It can be explained that the carboxylate oxygen atoms of ligands do not take part in the coordination with magnesium atoms[19]. The new band at 389 cm^{-1} is assigned to the ν(Mg-O) vibration. The band corresponding to the ν(OH) at 3 402 cm^{-1} shows that the complex contains water molecule, which is in accordance with the result of elemental analysis.

2.3 Crystal structure of complex

Perspective view of the molecule in a unit cell and molecular packing arrangement are shown in Fig.1. Selected bond distances and angles are listed in Table 2.



Symmetry codes: A: $-x$, $-y$, $-z$+1

Fig.1 Crystal structure of the complex

The title compound crystallizes in monoclinic system, space group $P2_1/c$. From Fig.1, it can be seen that the Mg(Ⅱ) center is six-coordinate with six oxygen atoms from the water molecules, and making up a distorted octahedral structure. The coordination atoms (O(1), O(3A), O(4), O(4A)) are situated equatorial place, and the coordination atoms (O (5), O (5A)) are situated

Table 2　Selected bond lengths (nm) and angles (°) of complex

Mg(1)-O(3)	0.203 3(2)	Mg(1)-O(4)	0.203 4(2)	Mg(1)-O(5)	0.209 7(3)
Mg(1)-O(3A)	0.203 3(2)	Mg(1)-O(4A)	0.203 4(2)	Mg(1)-O(5A)	0.209 7(3)
O(3)-Mg(1)-O(3A)	180.0	O(4)-Mg(1)-O(4A)	180.0	O(3)-Mg(1)-O(5A)	91.42(13)
O(3)-Mg(1)-O(4)	89.76(11)	O(3)-Mg(1)-O(5)	88.58(13)	O(3A)-Mg(1)-O(5A)	88.58(13)
O(3A)-Mg(1)-O(4)	90.24(11)	O(3A)-Mg(1)-O(5)	91.42(13)	O(4)-Mg(1)-O(5A)	87.87(14)
O(3)-Mg(1)-O(4A)	90.24(11)	O(4)-Mg(1)-O(5)	92.13(14)	O(4A)-Mg(1)-O(5A)	92.13(14)
O(3A)-Mg(1)-O(4A)	89.76(11)	O(4A)-Mg(1)-O(5)	87.87(14)	O(5)-Mg(1)-O(5A)	180.0

Symmetry codes: A: $-x$, $-y$, $-z+1$.

axial place. The distances of the Mg-O bonds are in the range of 0.203 3(2)~0.209 7(3) nm, respectively. They differ only slightly and are similar to the Mg-O bond lengths reported previously[20-23]. The benzene rings in the molecule do not show any unusual features, and the bond lengths and bond angles are within the range of normal values.

Fig.2 displays the molecular forms of 2D layered structure through intramolecule and intermolecule hydrogen bonds, the hydrogen bonds data are listed in Table 3. Hydrogen bonds are still rich in the complex, which may be divided into three sections according to the acceptors: (1) oxygen acceptors from carboxylic acids: N3–H3B⋯O1, O3–H9⋯O2, O3–H10⋯O1, O4–H11⋯O2; (2) nitrogen acceptors from the free 2-(thiosemicarbazonomethyl)benzoato: N3–H3A⋯N1; (3) sulfur acceptors from the free 2-(thiosemicarbazonomethyl)benzoato: N2–H2⋯S1, O3–H3A⋯S1, O5–H13⋯S1. The free 2-(thiosemicarbazonomethyl)benzoato forms hydrogen bonds with the coordinated water molecules, and play a role in connecting the coordinated groups through the oxygen atoms and nitrogen atoms which lies in the two ends of them. As a result of many intramolecular and intermolecular hydrogen bonds and the π-π packing interaction, the complex forms steady two dimensional layered structure (Fig.2).

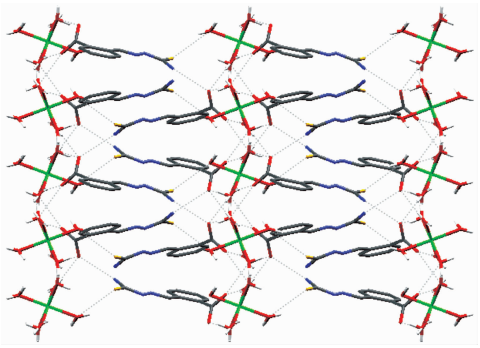


Fig.2　Two dimensional layered structure of the complex

Table 3　Hydrogen bonds data of the complex

D–H⋯A	D-H / nm	H⋯A / nm	D⋯A / nm	∠D-H-A / (°)
N(2)–H(2)⋯S(1)	0.086	0.256 4	0.340 3	165.2
N(3)–H(3A)⋯N(1)	0.086	0.226 8	0.262 2	104.8
N(3)–H(3A)⋯S(1)	0.086	0.285 1	0.353 9	138.3
N(3)–H(3B)⋯O(1)	0.086	0.207 8	0.289 5	158.3
O(3)–H(9)⋯O(2)	0.085	0.183 5	0.267 4	168.6
O(3)–H(10)⋯O(1)	0.085	0.199 8	0.284 0	171.5
O(4)–H(11)⋯O(2)	0.085	0.217 1	0.276 6	126.9
O(5)–H(13)⋯S(1)	0.085	0.261 6	0.322 0	129.0

2.4　Antibacterial activity

The antibacterial activity of the ligand and Mg(Ⅱ) complex were assayed using three positive (*escherichia coli*, *bacillus subtilis*, *staphylococcus white*) bacterial strains. The antibacterial results of the complex are listed in Table 4, and the results indicate that the Mg(Ⅱ) complex shows considerable antibacterial activity. Compared with the complex, the ligand did not show antibacterial activity. So the complex will provide potential applications in the broad spectrum of the

antibacterial field.

Table 4 MIC and MBC of complex against three bacterial strains

Strains	MIC / (mg·mL^{-1})	MBC / (mg·mL^{-1})
Escherichia coli	0.675	0.625
Bacillus subtilis	0.675	1.25
Staphylococcus white	0.675	0.625

MIC: minimal inhibitory concentration;
MBC: minimal bactericidal concentration.

3 Conclusions

According to the data and discussion above, TCB and water molecules have formed stable complex with magnesium. Obvious IR spectrum changes were observed after the ligand formed complex with magnesium. The crystal data of the complex shows that the magnesium atoms were coordinated to the oxygen atoms of water molecules. The complex formed two dimensional layered structure through intramolecule and intermolecule hydrogen bonds and π-π stacking. From the antibacterial results, we can see that the Mg(Ⅱ) complex shows considerable antibacterial activity against *escherichia coli*, *bacillus subtilis* and *staphylococcus white*, and the ligand did not show antibacterial activity. Based on those results, a series of new magnesium complexes would be designed and synthesized to investigate further the spectral properties and antibacterial activities.

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