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Article

Synthesis, Crystal Structure and Antibacterial Activity of Mg(II) Complex $[Mg(H_2O)_6]\cdot(4\text{-amino-3-methylbenzenesulfonate})_2$

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Abstract: A Mg(II) complex, $[Mg(H_2O)_6]\cdot L_2$ (H_2L = 4-amino-3-methylbenzenesulfonate), has been synthesized and characterized by elemental analysis, Infrared (IR) and single-crystal X-ray diffraction. The results indicated that the Mg(II) complex was monoclinic with $P2_1/n$, a = 6.3184(16) Å, b = 7.0522(18) Å, c = 24.434(6) Å, β = 93.946(3)°, V = 1086.2(5) Å^3, Z = 2, Mr = 504.81, Dc = 1.544 g/cm^3, T = 296(2) K, $F(000)$ = 532, μ(MoKa) = 0.338 mm^{-1}, R = 0.0339 and wR =0.1194. The Mg(II) ion lies in a distorted octahedral geometry. The hydrogen bonds and π-π stacking interaction play an important role in the forming of one dimensional chain structure. The antibacterial activity against *Escherichia coli*, *Bacillus subtilis* and *Staphylococcus white* of the Mg(II) complex has also been investigated.

Keywords: 4-amino-3-methylbenzenesulfonate; Mg(II) complex; synthesis; structural characterization; antibacterial activity

1. Introduction

During the past few years, inorganic-organic materials have drawn much interest in coordination chemistry because of their easy synthesis and good applications [1–5]. Many coordination compounds show considerable and important applications in luminescence, antibacterial and antitumor agents [6–10]. Relative to other metal cations, Mg(II) ion is an important element for biology [11,12]. It has taken part

in many process of life activity and played an important role the activation of enzymes. In contrast, Mg complex materials have not attracted attention. In our previous work, we have synthesized a series of Mg complex materials that display biological activities [13–15]. In this paper, we synthesize a Mg(II) complex by the reaction of 4-amino-3-methylbenzenesulfonate, $MgCl_6 \cdot 6H_2O$ and NaOH. The Mg(II) complex was characterized by elemental analysis, single-crystal X-ray diffraction and infrared spectroscopy, and the antibacterial activities of Mg(II) complex have also been investigated.

2. Results and Discussion

2.1. Elemental Analysis and IR Spectra

The result of elemental analysis indicates the composition of the Mg(II) complex as $[Mg(H_2O)_6] \cdot L_2$, which is in accord with the result of structural analysis. The IR spectrum of Mg(II) complex was also investigated, the broad band at *ca.* 3280 cm^{-1} corresponding to the *v* (OH) shows that the Mg(II) complex contains water molecule. The *v* (SO_3^-) vibrations of the free ligand are at 1675 cm^{-1}, 1208 cm^{-1} and 1044 cm^{-1}, respectively. For the complex, the vibrations were observed at 1676 cm^{-1}, 1206 cm^{-1} and 1043 cm^{-1}, which shows that the O atoms of SO_3^- group do not coordinate to Mg (II) atoms [16].

2.2. Description of $[Mg(H_2O)_6] \cdot L_2$

Single crystal X-ray analysis reveals that the Mg(II) complex molecule contains one Mg(II) cation, two L ligands and six coordinated water molecules. The molecular structure of Mg(II) complex is shown in Figure 1. As shown in Figure 1, the Mg(II) center is six-coordinated by six O atoms from six coordinated water molecules and forms a distorted octahedral coordination environment. The SO_3^- group and NH_2 group of H_2L do not take part in coordination with Mg(II) cations. The Mg-O lengths are in the range of 2.0335(14) Å–2.0815(12) Å. The angles around the Mg (II) center are O4-Mg1-O4A, 180.0(10)°; O4-Mg1-O5A, 88.34(5)°; O4A-Mg1-O5A, 91.66(5)°; O4-Mg1-O5, 91.66(5)°; O5-Mg1-O4A, 88.34(5)°; O5-Mg1-O5A, 180.0(5)°; O4-Mg1-O6, 89.48(5)°; O4A-Mg1-O6, 90.52(5)°; O5A-Mg1-O6, 87.51(6)°; O6-Mg1-O5, 92.49(6)°; O4-Mg1-O6A, 90.52(5)°; O4A-Mg1-O6A, 89.48(5)°; O5A-Mg1-O6A, 92.49(6)°; O6A-Mg1-O5, 87.51(6)°; O6A-Mg1-O5, 87.51(6)°; O6A-Mg1-O6, 180.0(7)°, respectively. The molecules display strong intramolecular and intermolecular hydrogen bonds (O–H···O) between the coordinated water molecules and the SO_3^- (Figure 2). The adjacent benzene rings of L ligands are contacted with each other though π-π interaction (Figure 3).

The Mg(II) complex molecules form a 1D chained structure by hydrogen bonds and π-π stacking interaction (Figures 2 and 3), and the hydrogen bonds and π-π stacking interactions increase the stability of the whole crystal structure.

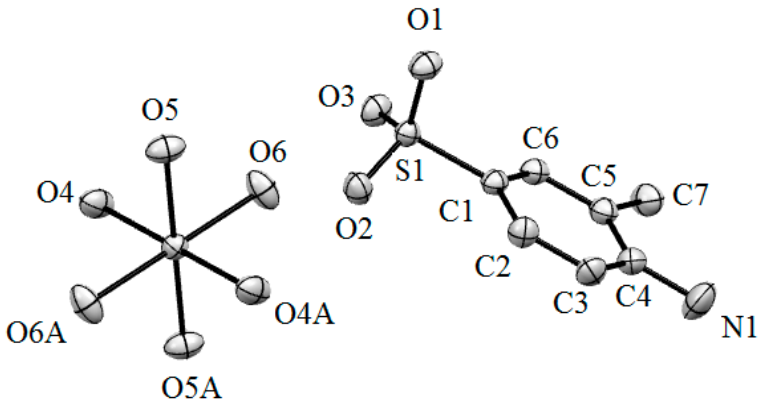

Figure 1. Molecular structure of the Mg(II) complex.

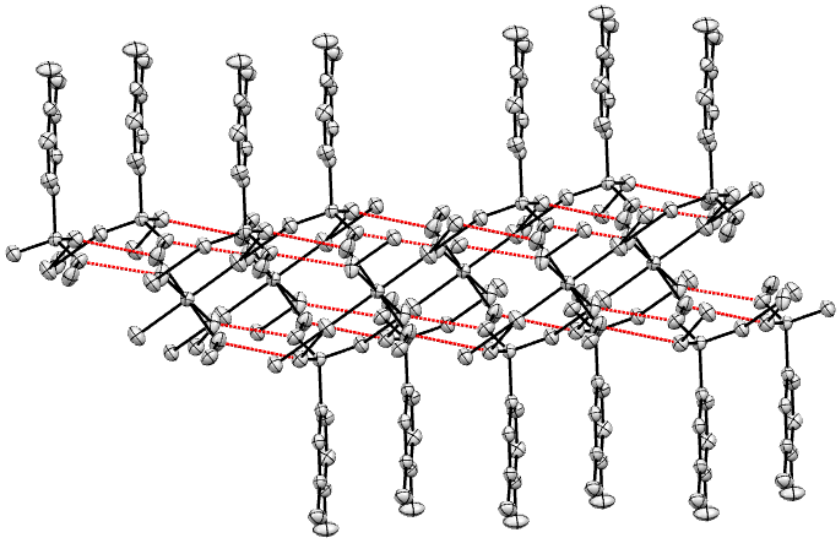

Figure 2. Hydrogen bonds interaction of Mg(II) complex.

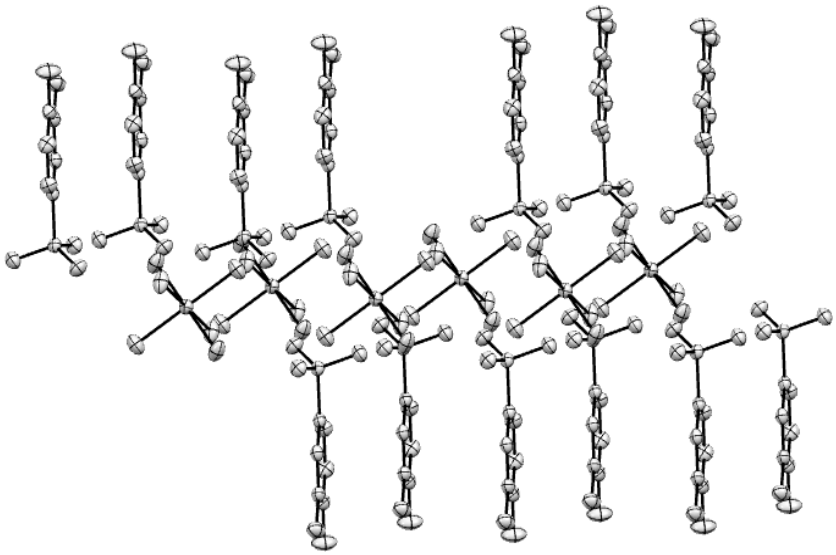

Figure 3. π-π stacking interaction of the Mg(II) complex (the diatance of adjacent benzene rings is 2.284 Å).

2.3. Antibacterial Activity

The antibacterial activities of the Mg (II) complex against *Escherichia coli*, *Bacillus subtilis* and *Staphylococcus white* were studied as references [11]. The antibacterial effects of Mg(II) complex are given in Table 1, the results show that the Mg (II) complex exhibits considerable antibacterial activity. Additionally, the antibacterial effects of $[Mg(H_2O)_6]\cdot L_2$ are better than that of other Mg(II) complexes [13,14].

Table 1. The antibacterial activity of the Mg (II) complex.

Strains	MIC/(mg·mL^{-1})	MBC/(mg·mL^{-1})
Escherichia coli	0.565	0.625
Bacillus subtilis	0.525	0.875
Staphylococcus white	0.475	0.975

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

3. Experimental Section

3.1. Materials and Instrumentation

For the experiment, 4-amino-3-methylbenzenesulfonate, $MgCl_6\cdot 6H_2O$, NaOH and solvents were used without further purification. Elemental analyses (for C, H and N) were carried out on an Elementar Vario EL III elemental analyzer. The IR spectra (4000–400 cm^{-1}) were recorded on a Nicolet AVATAR 360 FTIR spectrophotometer using the KBr pellet method. The crystal data collection was performed on a Bruker smart CCD Area Detector.

3.2. Preparation of $[Mg(H_2O)_6]\cdot L_2$

A total of 1.0 mmol (0.1862 g) of 4-amino-3-methylbenzenesulfonate, 1.0 mmol (0.0400 g) of sodium hydroxide and 0.5 mmol (0.1015 g) of $MgCl_6\cdot 6H_2O$ were added to the 10 mL of H_2O/CH_3CH_2OH (v:v = 1:1) solution. The above solution was stirred at 70 °C for 5 h. Then, the mixture was cooled to room temperature, and the single crystal suitable for X-ray determination was obtained by evaporation of the filtrate after 30 days at room temperature. Yield 62%. Anal. Calcd. for $C_{14}H_{28}MgN_2O_{12}S_2$: C, 33.28; H, 5.55; N, 5.55. Found: C, 33.62; H, 5.16; N, 5.88.

3.3. Crystal Structure Determination

The crystal data, data collection and refinement parameters for Mg(II) complex are given in Table 2, and the selected bond lengths and bond angles are listed in Table 3. The diffraction data were carried out on a Bruker Smart Apex CCD diffractometer (Bruker Company, Karlsruhe, Germany) with Mo$K\alpha$ radiation and φ–ω scan mode at 296 (2) K. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXL-97 [17]. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed in the calculated positions and assigned fixed isotropic thermal parameters. A total of 4858 reflection data were collected in the range of 3.01–25.10°, and 1911 were unique (R_{int} = 0.0169) and 1757 were observed with $I > 2\sigma(I)$. The SHELXTL-97 [18]

program package was used to refine structure and draw molecular graphics. The final refinement shows $R = 0.0339$, and $wR = 0.1194$ ($w = 1/[\delta^2(Fo^2) + (0.1000P)^2 + 0.0000P]$, $P = (Fo^2 + 2Fc^2)/3$).

Table 2. Summary of crystal results for the Mg(II) complex.

Formula	**$C_{14}H_{28}MgN_2O_{12}S_2$**
Formula weight	504.81
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	6.3184(16)
b (Å)	7.0522(18)
c (Å)	24.434(6)
β (°)	93.946(3)
Z	2
F(000)	532
Temperature (K)	296(2)
V (Å^3)	1086.2(5)
Calculated density (μg·m^{-3})	1.544
Crystal size (mm^3)	0.22 × 0.21 ×0.20
μ (mm^{-1})	0.338
S	1.062
Limiting indices	$-26 \leqslant h \leqslant 26$, $-6 \leqslant k \leqslant 6$, $-25 \leqslant l \leqslant 26$
Reflections collected	1.062
Unique reflections	1911
Parameters	166
Restraints	6
R_{int}	0.0169
R_1, wR_2 [all data]	0.0361, 0.1224
R_1, wR_2 [$I > 2\sigma(I)$]	0.0339, 0.1194
Largest diff.peak and hole (e·Å^{-3})	0.238, −0.691

Table 3. Selected bond lengths (Å) and angles (°) for the title compound.

Bond	**Distance**
Mg1-O4	2.0335(14)
Mg1-O4A	2.0335(14)
Mg1-O5	2.0761(12)
Mg1-O5A	2.0761(12)
Mg1-O6	2.0815(12)
Mg1-O6A	2.0815(12)
N1-C4	1.3735(19)
S1-O1	1.4637(11)
S1-O2	1.4582(12)
S1-O3	1.4612(13)

Table 3. *Cont.*

Angle	(°)
O4-Mg1-O4A	180.00(10)
O4-Mg1-O5A	88.34(5)
O4A-Mg1-O5A	91.66(5)
O4-Mg1-O5	91.66(5)
O5-Mg1-O4A	88.34(5)
O5-Mg1-O5A	180.00(5)
O4-Mg1-O6	89.48(5)
O6-Mg1-O4A	90.52(5)
O6-Mg1-O5A	87.51(6)
O5-Mg1-O6	92.49(6)
O4-Mg1-O6A	90.52(5)
O6A-Mg1-O4A	89.48(5)
O5A-Mg1-O6A	92.49(6)
O5-Mg1-O6A	87.51(6)
O6-Mg1-O6A	180.00(7)
O2-S1-O3	112.35(6)
O2-S1-O1	111.48(8)
O3-S1-O1	111.75(6)

Symmetry code: $-x, -y + 2, -z$.

4. Conclusions

In summary, an Mg(II) complex, $[Mg(H_2O)_6]\cdot L_2$ (H_2L = 4-amino-3-methylbenzenesulfonate), has been synthesized and characterized by elemental analysis, IR and single-crystal X-ray diffraction. The results indicated that the hydrogen bonds and π-π stacking interaction play an important role in the forming of one dimensional chain structure. The Mg(II) complex exhibits considerable antibacterial activity. Thus, more and more Mg(II) complexes will be synthesized to study their structures and antibacterial activities.

Acknowledgments

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Author Contributions

Xi-Shi Tai designed the method and wrote the manuscript. Yin Jie analyzed the crystal data for the Mg(II) complex and wrote the manuscript. Both authors have read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

Supplementary Materials

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No.CCDC 1413661. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

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