Studii şi Cercetări Ştiinţifice 2014, **15** (3), pp. 261 – 267
Chimie şi Inginerie Chimică, Biotehnologii, Industrie Alimentară

Scientific Study & Research
Chemistry & Chemical Engineering, Biotechnology, Food Industry *ISSN 1582-540X*

ORIGINAL RESEARCH PAPER

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF A NOVEL Mg(II) COMPLEX WITH 1,2-PHENYLENEDIOXYDIACETIC ACID

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Received: August, 05, 2014
Accepted: September, 29, 2014

Abstract: A novel Mg(II) complex, $[Mg(HL)_2\cdot(H_2O)_4]\cdot 4H_2O\cdot HCl$ (HL = 1,2-phenylenedioxydiacetato), has been synthesized by the reaction of 1,2-phenylenedioxydiacetic acid, NaOH and $MgCl_2\cdot 6H_2O$ in one-pot. The compound was characterized by X-ray single crystal diffraction analysis. The crystal of the title complex belongs to monoclinic, space group P_n with a = 10.772(2) Å, b = 9.7145(19) Å, c = 13.996(3) Å, β = 104.32(3)º, V = 1419.1(5) Å^3, Z = 2, Dc = 1.498 μg·m^{-3}, μ = 0.245 mm^{-1}, F(000) = 658 and final R_1 = 0.0653, ωR_2 = 0.1913. The molecules are connected by π-π stacking to form three dimensional network structures.

Keywords: *Mg(II) complex, 1,2-phenylenedioxydiacetic acid, structural characterization, synthesis*

INTRODUCTION

During the past decade, many attentions have been focused on the metal complexes, because they have some potential applications in molecular architectures, catalysis, biological chemistry, luminescent materials and electrochemistry [1 - 10]. Relative to other metal cations, magnesium is indispensable elements in biology [11, 12]. It is involved in several biochemical processes and is essential cofactors required for the activation of a variety of enzymes. By contrast, magnesium complexes have received much less attention. In our previous work, we have synthesized a series of magnesium complexes which display luminescence and antitumor activity [13 - 15]. As a part of our studies on synthesis, crystal structure and properties of Mg(II) complexes, we reported herein the synthesis and structural characteristic of a novel Mg(II) complex with 1,2-phenylenedioxydiacetic acid (H_2L).

EXPERIMENTAL

Materials and methods

1,2-Phenylenedioxydiacetic acid, $Mg(Cl)_2 \cdot 6H_2O$ and all the other solvents were of analytical grade and used without further purification. The experiments were carried out in open air. The crystal data was collected on a Bruker smart CCD Area Detector.

Synthesis of the Mg(II) complex

A methanol solution of 1.0 mmol (0.203 g) $MgCl_2 \cdot 6H_2O$ was added to a solution containing 1.0 mmol (0.226 g) of 1,2-phenylenedioxydiacetic acid and 2.0 mmol (0.040 g) of sodium hydroxide in 10 mL CH_3OH/H_2O (v:v = 1:1). The mixture was continuously stirred for 5 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 20 days.

X-ray Crystallography

A colorless block single crystal with dimensions of 0.24×0.22×0.20 mm was selected for measurement. Diffraction data of the single crystal were collected by φ~ω scan mode using a graphite-monochromatic Mo $K\alpha$ radiation (λ = 0.71073 Å) at 293(2) K on a Bruker Smart Apex CCD diffractometer. A total of 8887 reflections were collected in the range 2.58-28.49°, of which 5782 were unique (R_{int} = 0.0154) and 4731 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 = 0.0653, and wR = 0.1913 (w = $1/[\delta^2(Fo^2)+(0.1000P)^2+0.0000P]$, P = $(Fo^2+2Fc^2)/3$, S = 1.559). Molecular

graphics were drawn with the program package SHELXTL-97 crystallographic software package [17]. The most relevant crystal data for the title compound are quoted in Table 1, and the selected bond distances and angles are listed in Table 2 and 3.

Table 1. *Crystallographic data for the title compound*

Formula	$C_{20}H_{35}ClMgO_{20}$
Formula weight	640.12
Crystal system	monoclinic
Space group	P_n
a (Å)	10.772(2)
b (Å)	9.7145(19)
c (Å)	13.996(3)
β (º)	104.32(3)
Z	2
F(000)	658
Temperature (K)	293(2)
V (Å^3)	1419.1(5)
Calculated density (μg·m^{-3})	1.498
Crystal size (mm^3)	0.24×0.22×0.20
μ (mm^{-1})	0.245
S	1.559
Limiting indices	$-13 \le h \le 13$, $-12 \le k \le 6$, $-17 \le l \le 16$
Reflections collected	8887
Unique reflections	5782
Parameters	383
Restraints	2
R_{int}	0.0154
R_1, wR_2 [all data]	0.0805, 0.2131
R_1, wR_2 [I>2σ(I)]	0.0653, 0.1913
Largest diff.peak and hole (e·Å^{-3})	1.731, -0.487

Table 2. *Selected bond lengths for the title compound*

Bond	**Distance *(Å)***	**Bond**	**Distance *(Å)***
Mg1-O15	2.060(5)	Mg1-O16	2.066(5)
Mg1-O11	2.074(6)	Mg1-O14	2.085(5)
Mg1-O3	2.099(5)	Mg1-O13	2.121(5)
C9-O2	1.225(7)	C9-O3	1.255(7)
C19-O11	1.249(7)	C19-O12	1.283(8)
C1-O1	1.403(7)	C8-O6	1.257(8)
C8-O5	1.219(8)	C11-O10	1.352(8)
C20-O10	1.453(8)	C18-O9	1.246(7)
C18-O8	1.276(8)		

Table 3. *Selected angles for the title compound*

Angle	(°)	Angle	(°)
O15-Mg1-O16	179.8(3)	O11-Mg1-O16	92.7(2)
O15-Mg1-O11	87.2(2)	O15-Mg1-O14	90.1(2)
O14-Mg1-O16	90.0(2)	O11-Mg1-O14	87.9(2)
O15-Mg1-O3	92.7(2)	O3-Mg1-O16	87.4(2)
O11-Mg1-O3	179.0(3)	O14-Mg1-O3	93.1(2)
O15-Mg1-O13	91.2(2)	O13-Mg1-O16	88.7(2)
O11-Mg1-O13	91.7(2)	O14-Mg1-O13	178.6(3)
O3-Mg1-O13	87.3(2)	C11-O10-C20	117.9(6)
C1-O1-C10	116.1(5)	C2-O4-C7	121.3(4)
C12-O7-C17	113.7(5)		

RESULTS AND DISCUSSION

Structure Description

The molecular structure and perspective view of the crystal packing in the unit cell of the Mg(II) complex are shown in Figure 1 and Figure 2, respectively. Single-crystal X-ray diffraction study reveals that the Mg(II) complex crystallizes in monoclinic system with P_n space group. As shown in Figure 1, it can see that the Mg(II) adopts a distorted octahedral coordination with two oxygen atoms from two 1,2-phenylenedioxydiacetic acid ligands and four oxygen atoms from four coordinated water molecules.

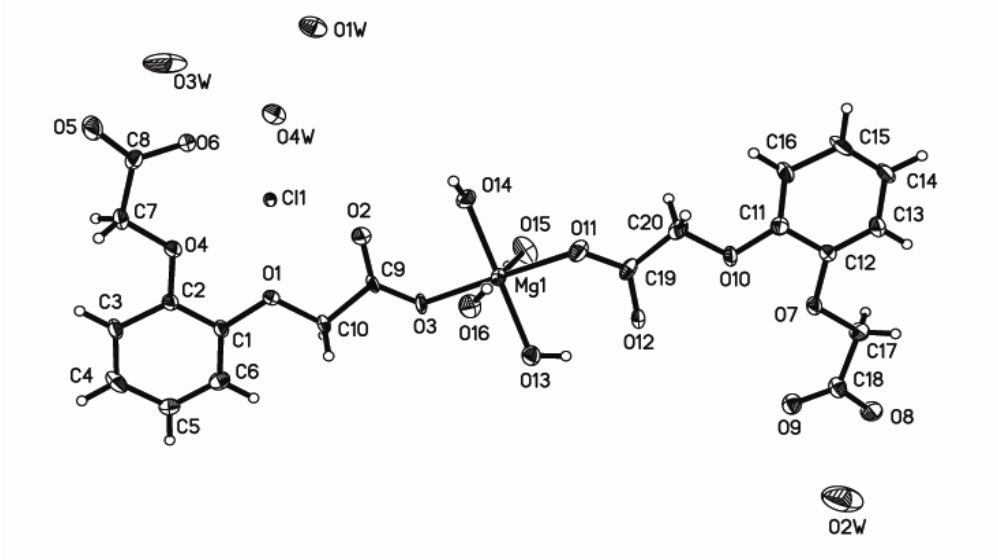

Figure 1. *Molecular structure of the Mg(II) complex, where the thermal ellipsoids were drawn at 30 % possibility*

In the Mg(II) complex, the carboxylates adopt monodentate coordination ways. The aromatic rings of two 1,2-phenylenedioxydiacetic acid ligands in the complex are nearly parallel, the dihedral angle and distance between ring 1 (C1-C6) and ring 2 (C11-C16) are 1.1°. The distances of the Mg-O bonds are in the range of 2.060(5)~2.121(5) Å, which is are similar to the Mg-O bond lengths reported previously [18, 19]. The aromatic rings in the molecules do not show any unusual features, and the bond lengths and bond angles are within the range of normal values.

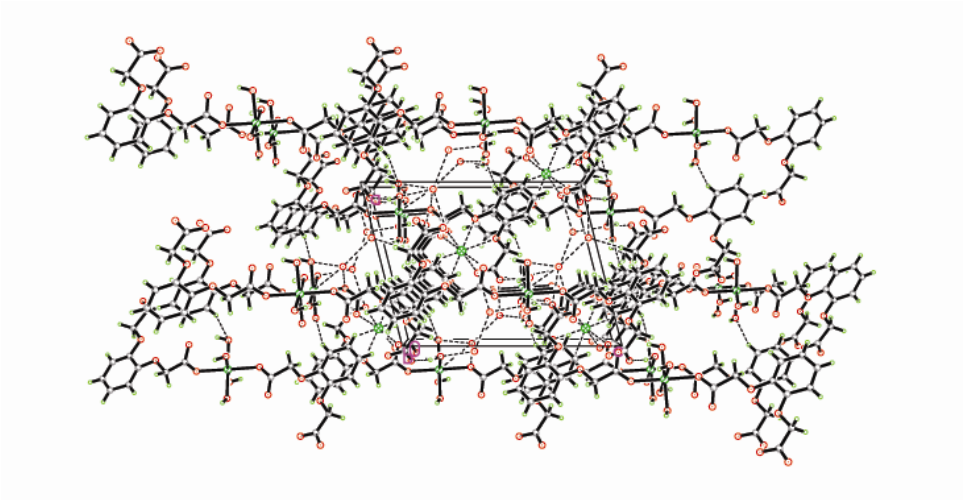

Figure 2. *Molecular packing of the Mg(II) complex*

The molecules stack with each other by π-π interaction in arrays to form a 3D network structure (Figure 3).

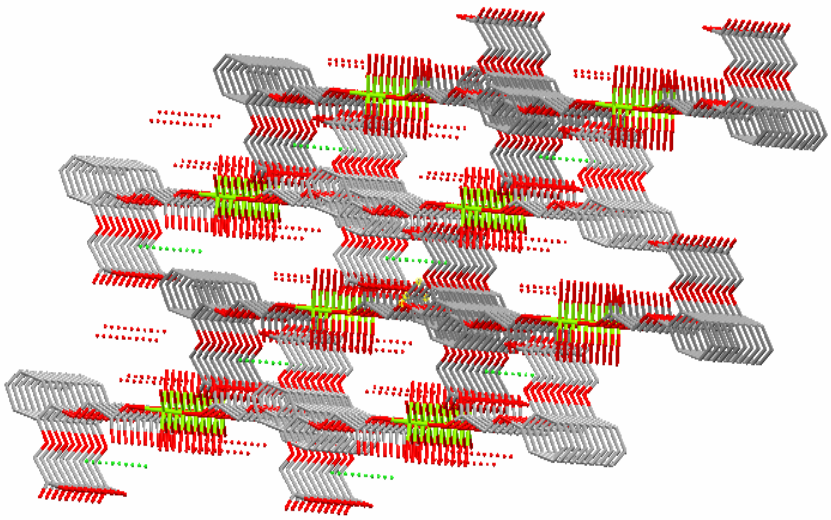

Figure 3. *3D network structure of the Mg(II) complex*

CONCLUSIONS

In summary, a novel Mg(II) complex has been synthesized and characterized by X-ray single crystal diffraction analysis. The results show that the molecules stack with each other by π-π interaction in arrays to form a 3D network structure.

ACKNOWLEDGMENTS

The authors would like to thank the National Natural Science Foundation of China (No. 21171132), the Project of Shandong Province Higher Educational Science and Technology Program (J14LC01) and Science Foundation of Weifang.

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