Send Orders for Reprints to reprints@benthamscience.ae

The Open Materials Science Journal, 2015, 9, 1-5

Open Access

Synthesis, Crystal Structure of Mg(II) Complex Material and its Application as Catalysts for A^3 Coupling Reaction

Xi-Shi Tai* and Li-Li Liu

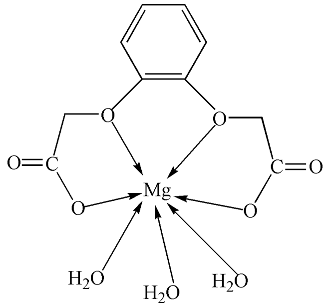
College of Chemistry and Chemical Engineering, Weifang University, Weifang 261061, China

Abstract: The ligand of 1, 2-phenylenedioxydiacetic acid (H_2L) has been employed to react with $MgCl_2{\cdot}6H_2O$ in water/ethanol solution (v:v = 1:1), to yield a novel Mg(II) complex $[MgL(H_2O)_3]{\cdot}3.5H_2O$. The complex was characterized by infrared spectroscopy and single crystal X-ray diffraction structural analysis. The results show that the Mg(II) complex belongs to monoclinic, space group C_2/c with a = 2.9160(6) nm, b = 0.67617(14) nm, c = 1.7319(4) nm, β = 109.06(3)°, V = 3.2275(11) nm^3, Z = 8, D_c= 1.562 $\mu g{\cdot}m^{-3}$, μ = 0.184 mm^{-1}, F (000) = 1560, and final R_1 = 0.0703, ωR_2 = 0.2256. The complex molecules form a 3D network structure through hydrogen bonds and π-π stack. The A^3 coupling reaction of phenylacetylene, aldehyde and amine (piperidine) in the presence of Au@Mg(II) complex as an efficient heterogeneous catalyst has been studied.

Keywords: 1,2-phenylenedioxydiacetic acid, catalytic property, crystal structure, Mg(II) complex, synthesis.

INTRODUCTION

Metal complex materials have been to attract the interest of chemists for many years, which may bring both intriguing architectures and promising potential applications in fields such as catalysis, gas storage, magnetics, luminescence materials, and so on [1-7]. In particular, aromatic carboxylic acid ligands play an important role in the construction of metal complex materials by their multiform coordination ways [8-12]. Early reports on aromatic carboxylate complexes are mostly focused on the transition metal complexes [13-15]. Magnesium ions take part in many biochemical activities in life. So the studies on the synthesis, structure and properties of Mg(II) complexes have important significance. With considering the points mentioned above, 1, 2-phenylenedioxydiacetic acid (H_2L) was chosen as the organic ligand to construct new Mg(II) complex materials. We report here the synthesis, crystal structure and catalytic property of a novel Mg(II) complex (Scheme **1**).



Scheme 1. The coordination mode Mg(II) ion.

EXPERIMENTAL SECTION

Materials and Methods

The 1,2-phenylenedioxydiacetic acid ligand, $MgCl_2{\cdot}6H_2O$, $HAuCl_4{\cdot}4H_2O$, 2,2-bipyridine, 1,4-dioxane, benzaldehyde, phenylacetylene, and piperidine were commercial materials of analytical grade.

C, H and N were carried out on Elementar Vario EL III elemental analyzer. The FT-IR spectra were obtained on a Nicolet AVATAR 360 FTIR spectrometer with KBr pellets in the range of 4,000 cm^{-1}~400 cm^{-1}. The catalytic products were quantified by GC analysis (GC-1100 equipped with a 0.25 mm×0.25 mm×30 m SE-54 capillary column). The single crystal diffraction data of the Mg(II) complex was collected on a Bruker smart CCD diffractometer.

Synthesis of Mg(II) Complex

Amounts of 0.5 m mol (0.1131 g) of H_2L, 1.0 m mol (0.040 g) of NaOH and 0.5 m mol (0.1015 g) of $MgCl_2{\cdot}6H_2O$ were dissolved in 10 mL of CH_3CH_2OH/H_2O (v:v = 1:1) solution. The mixture was reacted for 1.5 h at room temperature, then 0.5 mmol (0.0782 g) 2,2-bpy solid was added to the solution and the mixture was further heated for 3 h at refluxing temperature. The reaction mixture was filtrated. The crystals were obtained by evaporating methanol solution of Mg(II) complex. Elementary analysis: calcd for $C_{10}H_{21}MgO_{12.5}$: C, 32.88; H, 5.75; found: C, 33.16; H, 5.38. IR ν_{max} (cm^{-1}): ν(O-H): 3,250 cm^{-1}, $\nu_{as}(COO^-)$:1,638 cm^{-1}, $\nu_s(COO^-)$:1,442 cm^{-1}, ν(C-O-C): 1,220 cm^{-1}, ν(Mg-O):421 cm^{-1}.

X-Ray Crystallography

Suitable single crystals with approximate dimensions of 0.38 mm × 0.32 mm × 0.28 mm was mounted on a glass

---

*Address correspondence to this author at the College of Chemistry and Chemical Engineering, Weifang University, Weifang 261061, China;
E-mails: taixishi@Lzu.edu.cn, taixs@wfu.edu.cn

1874-088X/15 2015 Bentham Open

fiber and used for X-ray diffraction analyses. Data were collected on a Bruker smart CCD diffractometer at 273(2) K using a graphite-monochromatic Mo *Kα* radiation (λ = 0.71073 Å). The structure was solved by direct methods with SHELXL-97 [16]. The molecular graphics were drawn with the SHELXTL-97 program package [17]. The data collection and handling for the Mg(II) complex structure are listed in Table **1**. Important bond lengths and angles have been shown in Table **2**.

Table 1. The data collection and handling details for Mg(II) complex.

Formula	$C_{10}H_{11}MgO_{14}$
Formula weight	379.50
Crystal system	Monoclinic
Space group	C_2/c
a / nm	2.9160(6)
b / nm	0.67617(14)
c / nm	1.7319(4)
β(°)	109.06(3)
Z	8
F(000)	1560
Temperature (K)	293(2)
V / nm^3	3.2275(11)
Calculated density (μg·m^{-3})	1.562
Crystal size (mm^3)	0.38 × 0.32 × 0.28
Limiting indices	$-38 \leq h \leq 28$, $-8 \leq k \leq 8$, $-22 \leq l \leq 22$
Reflections collected/unique	9920 / 3142
Data/restraints/parameters	3887 / 0 / 226
R_{int}	0.0199
R_1, wR_2 (all data)	0.0818, 0.2361
R_1, wR_2 ($I > 2\sigma(I)$)	0.0703, 0.2256
Largest diff.peak and hole (e·nm^{-3})	849, −1192

Preparation of Au@Mg(II) Complex Catalyst (AMCC)

For synthesis of Au@Mg(II) complex catalyst by impregnation, a solution of $HAuCl_4 \cdot 4H_2O$ (0.020 g) in 0.5 ml MeCN was dropwise added to the Mg(II) complex support at room temperature and was sonicated for about 0.5 h. Then the sample was aged at room temperature for 12 h and dried at 50 °C for 10 h under air atmosphere. The as-synthesized sample was finally dried overnight at 323 K under air atmosphere to yield Au@Mg(II) complex catalyst.

Catalytic Measurements

Typical procedure for the A^3 coupling reaction: the mixture of benzaldehyde (0.25 mmol, 0.027 g), phenylacetylene (0.325 mmol, 0.034 g), piperidine (0.300 mmol, 0.026 g), and supported gold catalyst (0.07 g) were added into 1.500 g 1,4-dioxane. The mixture was reacted at 120 °C for 11 h. Then the catalysts were removed from the solution. The products were quantified by GC analysis (GC-1100 equipped with a 0.25 mm×0.25 mm×30 m SE-54 capillary column). The GC analysis conditions were as follows: initial column temperature 50°C, to 280 °C at 10 °C/min, and hold for 20 min.

Table 2. Selected bond lengths (Å) and angles (°) for Mg(II) complex.

Bonds	Bond Parameter	Bonds	Bond Parameter
Mg1-O1	0.2431(2)	Mg1-O7	0.2068(2)
Mg1-O2	0.2117(2)	Mg1-O8	0.2030(2)
Mg1-O4	0.23966(19)	Mg1-O9	0.2052(2)
Mg1-O5	0.21416(19)		
O1-Mg1-O4	62.50(6)	O2-Mg1-O5	160.89(8)
O1-Mg1-O5	130.97(7)	O7-Mg1-O5	80.85(7)
O1-Mg1-O2	67.80(7)	O9-Mg1-O5	86.92(8)
O7-Mg1-O1	148.01(8)	O8-Mg1-O5	90.03(9)
O1-Mg1-O9	88.44(8)	O2-Mg1-O7	80.77(8)
O1-Mg1-O8	85.96(9)	O2-Mg1-O9	90.48(8)
O4-Mg1-O5	68.49(6)	O2-Mg1-O8	95.63(9)
O2-Mg1-O4	129.94(7)	O9-Mg1-O7	97.88(9)
O4-Mg1-O7	149.28(8)	O7-Mg1-O8	91.58(9)
O4-Mg1-O9	82.78(8)	O9-Mg1-O8	169.47(9)
O4-Mg1-O8	86.72(8)		

RESULTS AND DISCUSSION

IR Spectra

The conspicuous COO$^-$ vibration of free ligand is at 1,718 cm^{-1} and 1,492 cm^{-1}, respectively. In the Mg(II) complex, they shift 80 cm^{-1} and 50 cm^{-1} towards lower wavenumbers, respectively, the C-O-C vibration is at 1,258 cm^{-1} in the free ligand, and appears at 1,220 cm^{-1} in the complex, all this indicating that the oxygen atoms of COO$^-$ and C-O-C coordinate to Mg(II) ions [18]. The strong peak at 3,250 cm^{-1} is ascribed to the O-H stretching vibrations of the coordinated and uncoordinated water. The ν (Mg-O) vibration band is observed at 421 cm^{-1}. Unfortunately, the 2,2-bpy ligand does not take part in coordination with Mg(II) ion, which is in accordance with the results of X-ray single crystal diffraction analysis.

Structure Description

The structural analysis shows that the Mg(II) complex crystallizes in the monoclinic, space group C_2/c. From Fig. (**1**), we can see that the Mg(II) cation is coordinated by four oxygen atoms from 1, 2-phenylenedioxydiacetic acid ligand (Mg1-O1 = 2.431(2) Å, Mg1-O2 = 2.1190(15) Å, Mg1-O4 = 2.3923(14) Å, Mg1-O5 = 2.1460(14) Å), and three oxygen atoms from coordinated water molecules (Mg1-O7 = 2.068(2) Å, Mg1-O8 = 2.030(2) Å, Mg1-O9 = 2.052(2) Å) in a distorted orthorhombic geometry. Also, the distances of Mg-O are comparable with that observed in other Mg-based complexes [19-21]. The molecules stack with each other *via* hydrogen bonds in arrays to form a 2D supramolecular structure (Figs. **2**, **3**).

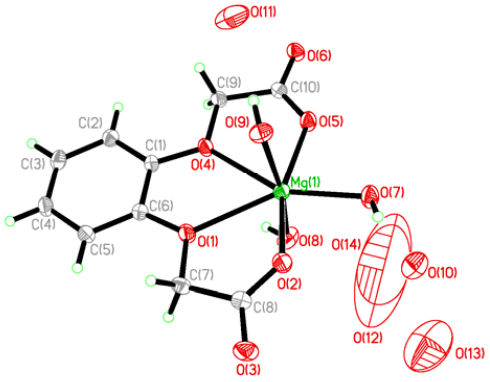


Fig. (1). The molecular structure of the Mg(II) complex.

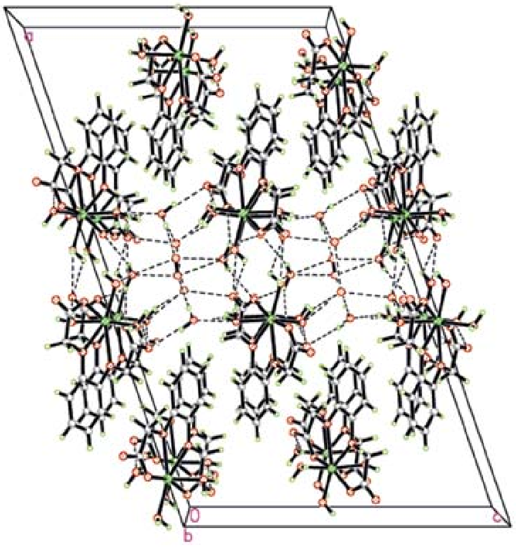


Fig. (2). The molecular packing arrangement of the Mg(II) complex.

Catalytic Properties

The catalytic performance of the Au@Mg(II) complex catalyst was assessed in the A^3 coupling reaction of benzaldehyde, phenylacetylene, and piperidine. The results are summarized in Table **3**. Effect of reaction temperature on the conversion of benzaldehyde over gold functionalized metal-organic frameworks was investigated (Table **3**, entries 1, 2). No higher than 2% conversion of benzaldehyde was found at the reaction temperature less than 80^{o}C, and a good conversion (94.1%) can be obtained at 120^{o}C. Gold functionalized Mg(II) complex catalysts feature 100% selectivity to the product of propargylamine for the A^3 coupling reaction.

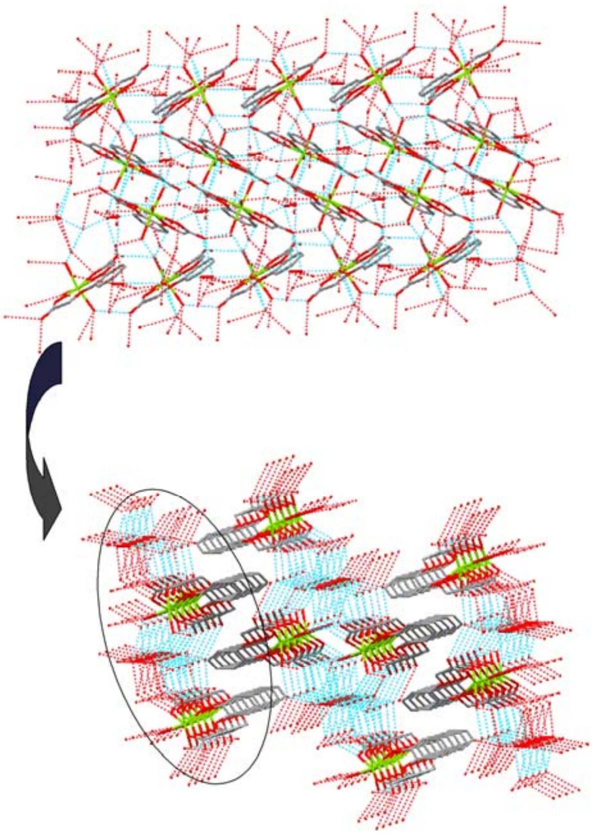
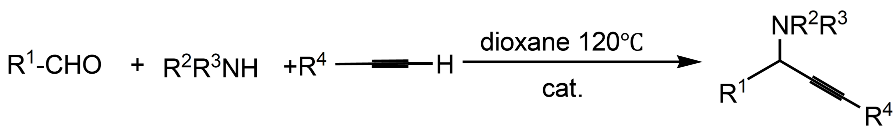


Fig. (3). Infinite 2D networks of Mg(II) complex.

To examine the scope of the A^3 coupling reaction, both aromatic aldehydes and aliphatic aldehydes were coupled with phenylacetylene and piperidine in the presence of Au@Mg(II) complex catalyst. Both aromatic aldehydes and aliphatic aldehydes were able to undergo the corresponding three-component-coupling, and afforded good conversions of aldehydes in the A^3 coupling reaction at 120 ^{o}C (Table **3**, entries 2-6). It was found that aromatic aldehydes possessing electron-withdrawing groups (Table **3**, entry 4) afforded higher conversions than aryl aldehydes with electron-donating groups bound to the benzene ring (Table **3**, entries 3) over Au@Mg(II) complex catalyst. Aliphatic aldehydes such as cyclohexanecarboxaldehyde and n-octaldehyde also display good to excellent conversions with the catalyst Au@Mg(II) complex (Table **3**, entries 5, 6).

The reusability studies of Au@Mg(II) complex catalyst were carried out on the A^3 coupling reaction of benzaldehyde, phenylacetylene, and piperidine at 120 ^{o}C. The results are summarized in Table **4**. The benzaldehyde converision is 94.1% within 11h at 120^{o}C over the fresh Au@Mg(II) complex catalyst. After three successive cycles with intermediate extensive washing with 1,4-dioxane, the conversions were 64.1%, 48.2%, and 47.6% at the reaction time of 18 h, 24 h, and 26 h, respectively. Clearly, the gold

Table 3. Coupling of aldehyde, alkyne, and amine catalyzed by Au@Mg(II) complex catalyst complex in dioxane[a].



Entry	Cat.	R^1	R^{2}R^{3}NH	R^4	T(°C))	T(h)	Conv.(%)
1	AMCC	Ph	piperidine	Ph	80	12	2.0
2	AMCC	Ph	piperidine	Ph	120	11	94.1
3	AMCC	4-MeC$_6$H$_4$	piperidine	Ph	120	11	16.3
4	AMCC	3-ClC$_6$H$_4$4	piperidine	Ph	120	11	75.3
5	AMCC	Cyclohexyl	piperidine	Ph	120	11	98.5
6	AMCC	Heptyl	piperidine	Ph	120	11	94.1

[a]Reaction conditions: aldehyde (0.250mmol), amine (0.300mmol), alkyne (0.325mmol), catalyst (0.07 g); [b]the reaction time was not optimization.

functionalized Mg(II) complex catalyst features a significant deactivation by around 30% for the first run, while further recycling leads to 15.9% and 0.6% deactivation.

Table 4. Recyclability of Au@Mg(II) complex catalyst in A^3 coupling reaction of benzaldehyde, piperidine, and phenylacetylene [a].

Run	Cat.	Time (h)	Conv. (%)	Selectivity (%)
Fresh	AMCC	11	93.1	100
1	AMCC	18	64.1	100
2	AMCC	24	48.2	100
3	AMCC	26	47.6	100

[a]Reaction conditions: benzaldehyde (0.250 mmol), piperidine (0.300 mmol), phenylacetylene (0.325 mmol), and dioxane (1.5 g), catalyst (0.07 g), 120 °C.

CONCLUSION

In summary, a Mg(II) complex material was prepared and characterized. In complex the two chains of carboxylate ligands exhibit different coordination modes. The molecules form two dimensional structures by the hydrogen bonds and π-π stack. In addition, the catalytic properties reveal that the Au@Mg(II) complex catalyst exhibits good conversion and selectivity for the A^3 coupling reaction.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

The authors would like to thank the National Natural Science Foundation of China (No. 21171132 and 20671073), the Project of Shandong Province Higher Educational Science and Technology Program (J14LC01) and Science Foundation of Weifang.

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 991526. 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).

REFERENCES

[1] Zhou XJ, Li BY, Li GH, *et al.* Synthesis, structures and luminescent properties of cadmium (II) metal organic frameworks based on 3-pyrid-4-ylbenzoic acid, 4-pyrid-4-ylbenzoicLigands. Cryst Eng Commun 2012; 14: 4664-9.

[2] Xu WJ, Xie ZJ, Zhang LY, *et al.* Synthesis, structures, characterization and antimicrobial activity of two novel coordination complexes derived from 2-naphthoxyacetic acid. J Iran Chem Soc doi: 10.1007/s13738-013-0401-7.

[3] Tai XS, Yin J, Feng YM, *et al.* Synthesis and crystal structure of Ca (II) complex with salicylaldehyde-4-aminobenzene sulfonic acid. Chin J Inorg Chem 2007; 23: 1812-4.

[4] Aurore T, Lydia KB, Dominique M. Coordination versatility and amide shift in mononuclear Fe^{II} complexes with the asymmetrical tripod [(6-bromo-2-pyridyl)methyl][(6-pivaloylamido-2-pyridyl)methyl](2-pyridylmethyl)amine (BrMPPA). Eur J Inorg Chem 2013; 2013: 1118-22.

[5] Mobec B, Zubieta J. Syntheses and a solid state structure of a dinuclear molybdenum(V) complex with pyridine. Materials 2010; 3: 150-7.

[6] Tai XS, Zhao WH. Synthesis, structural characterization, and antitumor activity of a Ca(II) coordination polymer based on 1,6-naphthalenedisulfonate and 4,4′-bipyridyl. Materials 2013; 6: 3547-55.

[7] Li Q, Wang Y, Yan PF, Hou GF, Li GM. Two 7,7,8,8-tetracyanoquinodimethane lead and zinc complexes featuring 3D and 0D structure: Synthesis, structure and electrochemical properties. Inorganica Chimica Acta 2014; 413: 32-7.

[8] Lu WG, Jiang L, Feng XL, *et al.* Three 3D coordination polymers constructed by Cd(II) and Zn(II) with imidazole-4,5-dicarboxylate and 4,4'-bipyridyl building blocks. Cryst Growth Des 2006; 6: 564-71.

[9] Tai XS, Jiang JH. Synthesis, crystal structure and luminescent property of Cd (II) complex with *N*-benzenesulphonyl-*L*-leucine. Materials 2012; 5: 1626-34.

[10] Wang LF, Hu YX, Zhang WW, *et al*. Solvothermal synthesis, crystal structure and photoluminescence property of a coordination polymer based on 1,1'-ethynebenzene-3,3',5,5'-tetracarboxylate. Chin J Inorg Chem 2011; 27: 542-6.

[11] Xu GH, Ma Y, Wang K, *et al*. Synthesis, structure, and magnetic properties of manganese-organic frameworks of 2-methyl-4,4′-biphenyldicarboxylate with different auxiliary ligands. J Mol Struct 2013; 1040: 25-32.

[12] Price DJ, Coles SJ, Hursthouse MB. Crystal structure of cobalt(II) 1,12-dodecanedioate trihydrate: a new layered coordination network. J Struct Chem 2013; 54: 474-8.

[13] Tai XS, Feng YM, Wang LT, *et al*. Synthesis, structure characterization and luminescent properties of ternary zinc acetate complex with 4-aminohippuric acid and1,10-phenanthroline ligand. Pol J Chem 2009; 83: 1099-104.

[14] Patra R, Goldberg I. A three-dimensional coordination polymer of 3-(3,5-dicarboxybenzyloxy)benzoic acid with zinc. Acta cryst 2013; C69: 819-21.

[15] Reger DL, Debreczeni A, Pascui AE. Heptanuclear zinc carboxylate complex: new supramolecular building unit and unique supramolecular architecture. Polyhedron 2013; 52: 1317-22.

[16] Sheldrick GM. SHELXL-97, Program for Crystal Structure Solution; University of GÖttingen: GÖttingen, Germany, 1997.

[17] Sheldrick GM. SHELXTL-97, Program for Crystal Structure Refinement; University of GÖttingen: GÖttingen, Germany, 1997.

[18] Nakamoto K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd ed. John Wiley and Sons: New York, NY, USA, vol.1, pp. 359-368, 1978

[19] Tai XS, Wei N, Wang DH. Synthesis, crystal structure and luminescent property of Mg (II) complex with *N*-benzenesulphonyl-L-leucine and 1,10-phenanthroline. Materials 2012; 5: 558-65.

[20] Tai XS, Du LC, Zhao ZB. Synthesis, crystal structure and antibacterial activity of magnesium (II) complex with *N*-benzenesulphonyl-*L*-phenylalanine and 1,10-phenanthroline. Chin J Inorg Chem 2011; 27: 575-9.

[21] Tai XS, Li YF, Zhao WH. Synthesis and crystal structure of Mg (II) complex with 3-amino-2-pyrazinecarboxylic acid ligand. J Chem Pharm Res 2014; 6: 516-20.

Received: August 21, 2014 Revised: December 21, 2014 Accepted: December 22, 2014

© Tai and Liu; Licensee *Bentham Open*.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (http://creativecommons.org/licenses/by-nc/3.0/) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.