Synthesis, spectral characterization, and luminescence properties of a cup-like ligand and its magnesium(II) complex

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Abstract A new tripodal ligand, N,N',N''-tri(salicylaldehyde)triaminotriethylamine (1) has been synthesized and characterized by elemental analysis, IR and UV spectroscopy, MS, and X-ray crystallography. X-ray diffraction analysis reveals that the three chains of the ligand form a cup-like structure. The ligand's magnesium(II) complex has been synthesized and characterized by elemental analysis, conductivity, and IR and UV spectroscopy. The luminescence properties of the ligand and its magnesium(II) complex were investigated in DMF, CH₃OH, and CH₃CH₂OH solution and in the solid state at room temperature.

Keywords Tripodal ligand · Magnesium(II) complex · Synthesis · Crystal structure · Luminescence properties

Introduction

Design and construction of inorganic–organic hybrid materials have attracted extensive interest in coordination chemistry because of their excellent functional properties, for example luminescence, magnetism, biological activity, and catalysis, and their variety of structures and topology [1-7]. Many studies of inorganic–organic hybrid materials have traditionally focused on transition metal and rare earth complexes [8–10]. Synthesis of inorganic–organic hybrid materials containing the magnesium(II) cation is rare [11-13]. Recently, we designed a series of Mg(II) complexes to investigate their properties. In this work, we

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designed and synthesized a new functionalized ligand with tripodal structure, N,N',N''-tri(salicylaldehyde)triaminotriethylamine (1), and its Mg(II) complex. The spectral and luminescence properties of ligand and its Mg(II) complex were also studied.

Experimental

Apparatus and reagents

Triaminotriethylamine, salicylaldehyde, $MgCl_2 \cdot 6H_2O$, and other chemicals were reagent grade and used without further purification.

Elemental analysis (C, H and N) was performed on a Elementar Vario EL III elemental analyzer. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4,000–400 cm⁻¹ region. Molar conductance was determined with a DDS-11A conductivity meter with methanol as solvent $(10^{-3} \text{ mol } \text{L}^{-1} \text{ solution})$ at 25 °C. Mass spectra were acquired by use of a ZAB-HS analyzer. UV–visible spectra were acquired by use of a Thermo UV-340 spectrometer in the range of 700–190 nm in CH₃CH₂OH solution. Luminescence spectra were obtained with a PE LS-55 fluorescence spectrophotometer.

Synthesis of the ligand

Salicylaldehyde (1.830 g, 15.0 mmol) was slowly added to a solution of triaminotriethylamine (0.730 g, 5.0 mmol) in ethanol (10 mL). The mixture was heated under reflux for 3 h with continuous stirring, then the resulting yellow precipitate was isolated by filtration, washed several times with ethanol, and dried in vacuo. Yellow crystals suitable for single crystal X-ray structure determination were obtained by slowly evaporating an ethanol solution of **1** at room temperature. Yield: 76 %. Anal. Calc. For $C_{27}H_{30}N_4O_3$ (%): C, 70.66; H, 6.54; N, 12.21. Found (%): C, 70.36; H, 6.37; N, 12.52. IR (KBr pellet; v_{max} cm⁻¹): 1,665 (s, C=N), 1,594 (m), 1,518 (m), 1,224 (s, C–O). MS (FAB): 459 (M + 1).

Synthesis of the Mg(II) complex

N,N',N"-tri(salicylaldehyde)triaminotriethylamine (0.458 g, 1.0 mmol) and sodium hydroxide (0.120 g, 3.0 mmol) were added to 15 mL CH₃CH₂OH. After dissolution, magnesium chloride (0.690 g, 3.0 mmol) was added to the solution. The mixture was continuously stirred for 2 h at reflux temperature. The mixture was then cooled to room temperature and the solid formed was isolated by filtration. Yield 58 %. Anal. Calcd. for C₅₄H₆₆Mg₃N₈O₁₂: C, 59.45; H, 6.06; N, 10.28. Found: C, 59.05; H, 6.32; N, 9.99. $\Lambda_{\rm m}$ (s cm² mol⁻¹): 8.9. IR $\nu_{\rm max}$ (cm⁻¹): 1,653 (s, C=N), 3,423 (m, H₂O), 1,592 (m), 1,517 (m), 1,203 (m, C–O).

X-ray crystallography

A vellow single crystal of dimensions 0.24 mm \times 0.20 mm \times 0.14 mm was placed on a glass fiber and mounted on a CCD area detector. Diffraction data were collected in $\varphi - \omega$ scan mode using graphite-monochromated Mo K α radiation $(\lambda = 0.71073 \text{ Å})$ at 298 K. A total of 22,522 reflections were collected in the range $3.10-27.50^\circ$, of which 5,698 were unique ($R_{int} = 0.040$) and 3,100 were observed with $I > 2\sigma(I)$. The data were corrected for Lp factors. The structure was solved by direct methods using SHELXL-97 [14] and expanded using Fourier techniques. All non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. Final refinement by the full-matrix least-squares method was converged at R = 0.0650, and wR = 0.1658 ($w = 1/[\delta^2(Fo^2) + (0.0841P)^2 +$ 0.3728P], $P = (Fo^2 + 2Fc^2)/3$, S = 1.127, $(\Delta/\sigma)_{max} = 0.000$). The largest peak in the final difference Fourier map is 0.394 e/Å³ and the minimum peak is -0.275 e/Å³. Molecular graphics were drawn with the crystallographic software package SHELXTL-97 [15]. The CCDC reference number is 894122. The most relevant crystal data for the ligand are listed in Table 1. The relevant bond lengths and bond angles are listed in Table 2.

Table 1Crystallographic dataand structure refinement for theligand

Crystal data	
Chemical formula	$C_{27}H_{30}N_4O_3$
Formula weight	458.55
Cell setting, space group	Monoclinic, P21/c
<i>a</i> (Å)	9.868 (2)
<i>b</i> (Å)	11.215 (2)
<i>c</i> (Å)	22.931 (5)
α (°)	90.00
β (°)	98.82 (3)
γ (°)	90.00
Volume (Å ³)	2,507.8 (9)
Ζ	4
$Dc (Mg m^{-3})$	1.215
Crystal size (mm)	$0.24 \times 0.20 \times 0.14$
Radiation (Å)	Μο Κα, 0.71073
Theta min-max (°)	3.10-27.50
Total, unique data, R(int)	22,522, 5,698, 0.040
Observed data $[I > 2.0 \text{ sigma}(I)]$	3,100
F (000)	976
R, wR_2, S	0.0650, 0.1658, 1.127
Min. and max. resd. dens. $(e/Å^3)$	0.394, -0.275

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Bond length (Å)						
C7-N2	1.270 (3)	C19-N1	1.458 (3)			
C8-N2	1.451 (3)	C20-N3	1.462 (3)			
C10-N1	1.469 (3)	C21-N3	1.266 (3)			
C11-N4	1.448 (4)	C18-O2	1.338 (3)			
C12-N4	1.270 (3)	C23–O3	1.345 (3)			
C9-N1	1.465 (4)					
Bond angle (°)						
C19-N1-C9	112.5 (2)	C12-N4-C11	121.1 (3)			
C19-N1-C10	112.1 (2)	O1-C5-C4	119.2 (3)			
C9-N1-C10	112.3 (2)	O2-C18-C17	119.1 (2)			
C7-N2-C8	120.0 (2)	O3-C23-C22	120.7 (2)			
C21-N3-C20	119.5 (2)					

Table 2 Selected bond lengths (nm) and angles (°) for the ligand

Results and discussion

Structure description

The molecular structure of ligand is shown in Fig. 1. It can be seen that the ligand has a cup-like structure with the tertiary amine nitrogen atoms lying at the bottom. The three chains make C9–N1–C19, C10–N1–C19, and C10–N1–C9 angles of 112.5(2), 112.1(2), and 112.3(2)°, respectively. The bond distances in the three chains, except those in the phenyl rings, are in the range of 1.499(4)–1.513(4) Å for C–C, 1.266(3)–1.270(3) Å for C=N, and 1.448(4)–1.469(3) Å for C–N. The bond lengths and bond angles of the benzene rings in the molecule are within normal



ranges. The crystal structure of the ligand is stabilized by intramolecular hydrogen bonds (Fig. 1).

Properties of the Mg(II) complex

Results from elemental analysis indicated that the composition of the Mg(II) complex was Mg_3L_2 ·6H₂O. The Mg(II) complex is soluble in DMF, DMSO, methanol, slightly soluble in ethanol and acetone, and insoluble in benzene, diethyl ether, and THF. The molar conductance of the Mg(II) complex measured in CH₃OH solution $(1 \times 10^{-3} \text{ mol } L^{-1})$ at 25 °C is 8.9 scm² mol⁻¹, showing the Mg(II) complex is a non-electrolyte [16].

IR spectra

The v (C=N) vibration of the free ligand is at 1,665 cm⁻¹ and for the Mg(II) complex shifts to 1,653 cm⁻¹, indicating that the nitrogen atoms of the C=N coordinate to the Mg(II) ions [17]. The band at 1,224 cm⁻¹ in the free ligand is assigned to v (C–O) vibration of phenolic group; it shifts to 1,203 cm⁻¹ in the complex, showing that oxygen atoms of phenolic hydroxyl coordinate to Mg(II) ions. In addition, the band at 3,423 cm⁻¹ shows that the complex contains water molecules, in accordance with results from elemental analysis.

UV spectra

The spectrum of the free ligand contains two absorption bands at 314 nm and 403 nm. The spectrum of the Mg(II) complex contains two absorption bands at 319 nm and 390 nm. These can be assigned to the π - π * and n- π * transitions.

Luminescence properties

The luminescence characteristics of the ligand and its Mg(II) complex in the solid state and in organic solvent are listed in Table 3. The emission spectra of the ligand

Compound	Solvent	λex (nm)	λem (nm)	R FI ^a
Ligand	Solid	329	505	17.3
	DMF	368	460	278.9
	CH ₃ OH	358	478	10.6
	CH ₃ CH ₂ OH	360	480	41.1
Mg(II) complex	Solid	326	517	27.4
	DMF	286	441	184.1
	CH ₃ OH	390	484	264.0
	CH ₃ CH ₂ OH	398	480	2,510.2

Table 3 Luminescence data for the ligand and its Mg(II) complex

^a *RFI* relative fluorescence intensity

and Mg(II) complex in the solid state and in organic solvent are shown in Figs. 2 and 3, respectively.

Table 3 and Fig. 2 indicate that maximum emission of the free ligand is at 505 nm when excited at 329 nm in the solid state. The effects of organic solvents on the fluorescence properties of the free ligand were tested. It is apparent that in organic solvents the maximum emission peak is blue shifted and the maximum excitation peak is red shifted. The solvents DMF and CH_3CH_2OH enhance the fluorescence intensity whereas CH_3OH reduces the fluorescence intensity.

Table 3 and Fig. 3 indicate that maximum emission of the Mg(II) complex is at 517 nm when excited at 326 nm in the solid state. Compared with that of the free ligand, the maximum emission peak is red shifted. The fluorescence quantum yield of the Mg(II) complex is 0.152 with quinine sulfate as reference. The solvents DMF, CH₃OH, and CH₃CH₂OH enhance the fluorescence intensity. This may not only be because of removal of the inner sphere of coordinating water molecules in the Mg(II) complex but also because of energy transfer from the organic solvents to N.N', N''-tri(salicylaldehyde)triaminotriethylamine. So, intramolecular energy transfer is a major factor in the process of enhancing the luminescence of this system [18]. The enhancing effect of organic solvents on the fluorescence of the Mg(II)complex is in the order $CH_3CH_2OH > CH_3OH > DMF$. The dielectric constants (ϵ) of these solvents are 37.6 (DMF), 32.6 (CH₃OH), and 24.3 (CH₃CH₂OH). The order of fluorescence intensities of the Mg(II) complex is contrary to the ε values of these organic solvents. CH₃CH₂OH has the strongest enhancing effect of these organic solvents. The dielectric constant and refractive index of the solvent are correlated with the Stokes shift. However, It can be assumed polarity is an important factor here.



Fig. 2 The emission spectra of the ligand in the solid state and in organic solvents $(1.0 \times 10^{-5} \text{ mol L}^{-1})$. The excitation and emission slit widths were 5 nm



Fig. 3 The emission spectra of the Mg(II) complex in the solid state and in organic solvents $(1.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$. The excitation and emission slit widths were 5 nm

Conclusions

In summary, we have synthesized a new tripodal ligand and its Mg(II) complex. The ligand has been characterized by elemental analysis, IR and UV spectroscopy, MS, and X-ray crystallography. Its magnesium(II) complex also has been synthesized and characterized by elemental analysis, conductivity measurement, and IR and UV spectroscopy. The results show that the Mg(II) ions are coordinated to the nitrogen and oxygen atoms of the ligand and to water molecules. The fluorescence properties of ligand and its Mg(II) complex were tested in the solid state and in organic solvents. On the basis of the results obtained a series of new Mg(II) complex can be synthesized to optimize the fluorescence properties.

Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 894122. A 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).

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References

- 1. L.Q. Zhou, F. Wang, Z.W. Tang, L.R. Zhou, J.T. Sun, Spectrosc. Lett. 43, 108 (2010)
- 2. T.F. Yan, M. Hong, L. Niu, F. Jiang, G.M. Xiao, Res. Chem. Intermed. 38, 1389 (2012)
- H.L. Wang, L.F. Zhang, Z.H. Ni, W.F. Zhong, L.J. Tian, J.Z. Jiang, Cryst. Growth Des. 10, 4231 (2010)
- 4. X.P. Yang, A.J. Richard, J. Am. Chem. Soc. 127, 7686 (2005)
- 5. W.C. Huang, C.C. Lin, Inorg. Chem. 48, 728 (2009)
- F.A. Bassyouni, S.M. Abu-Bakr, K.H. Hegab, W. El-Eraky, A.A. El Beih, M.E. Abdel Rehim, Res. Chem. Intermed. 38, 1527 (2012)
- 7. X.S. Tai, H.Q. Wang, X.Z. Sun, M.Y. Tan, Spectrosc. Lett. 38, 497 (2005)
- 8. Y. Wang, T. Wang, G.X. Liu, Y.C. Chen, Chin. J. Inorg. Chem. 26, 1467 (2010)
- 9. K.A. Kumar, K.L. Reddy, S. Satyanarayana, Spectrosc. Lett. 44, 27 (2011)
- 10. F.F. Jian, H.L. Xiao, P.P. Sun, P.S. Zhao, Molecules 9, 876 (2004)
- 11. X.S. Tai, N. Wei, D.H. Wang, Materials 5, 558 (2012)
- H.X. Deng, S. Grunder, K.E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gandara, A.C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O'keeffe, O. Terasaki, J.F. Stoddart, O.M. Yaghi, Science 336, 1018 (2012)
- 13. A. Erxleben, D. Schumacher, Eur. J. Inorg. Chem. 12, 3039 (2001)
- 14. G.M. Sheldrick, SHELXL-97 (University of Gottingen, Gottingen, 1997)
- 15. G.M. Sheldrick, SHELXTL-97 (University of Gottingen, Gottingen, 1997)
- 16. W.J. Geary, Coord. Chem. Rev. 7, 81 (1971)
- 17. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn. (Wiley, New York, 1978)
- 18. T.L. Yang, X.S. Tai, W.W. Qin, W.S. Liu, M.Y. Tan, Anal. Sci. 20, 357 (2004)