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Preparation, Structure and Fluorescence properties of Novel Zinc(II) Complex Containing taurine Schiff Base Ligand

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Abstract: In recent years, with Schiff base being applied and researched deeply in biology, IsoIsovanillinSchiff base ligands' synthesis and the coordinathion properties have become a hot spot in the research of Schiff bases compounds. This paper expounds that we keep Isovanillin and taurine as the raw material to design and synthesize Schiff base ligands, and Zinc(II) of metal compounds to form the corresponding Zn(II) complexes by solvent. The crystal structure of the Zinc(II) complex has been determined and studied by X-ray diffraction.

Introduction

Taurine has important physiological functions. It can promote brain tissue, intelligence and retina development, promote immune function and lipid digestion and absorption, protect myocardium and antioxidation in infants. Because of its unique pharmacological and physiological functions, it has been widely used in food, medicine and chemical industry. A lot of taurine complexes and the Taurine Schiff base metal complexes research reports, which formed at the same time sulfonate and the corresponding metal ions involved in hydrogen bonding, or just to participate in the formation of hydrogen bonds. A new type of complex ［$Zn(TISB)(phen)_2$］ was prepared by aqueous solution using TISB and phen as mixed ligands. Its structure is characterized by IR and X- ray single crystal diffraction.

Experimental

Materials and physical measurements

All solvents and chemicals purchased from commercial sources were of reagent grade and used without further purification. IR spectra were performed on a Shimizu spectrum FT-IR spectrometer with KBr pallets in the range of 4000 ～ 400 cm^{-1}.The elemental analyses for C, H, N and S were carried out on a Leeman elemental analyzer. The crystal data were collected on a Rigaku Xtalab area detector diffractometer at room temperature.

Synthesis of the ligand(L)

In the reaction flask, anhydrous methanol 80mL, taurine 2.5g (20 mmol) and KOH 0.112g (20 mmol) were added successively to dissolve them. A slow trickle of Isovanillin 3.04 g (20 mmol) of anhydrous methanol (20 mL) solution, drop after icewater cooling reaction under 4 h. The filter cake was placed in a stationary position and filtered. The cake was washed with anhydrous methanol (3 ×20 mL) and ether (3×20 mL) in a row. The vacuum dried yellow powder, TISB 4.22 g, was obtained with a yield of 71%. IRν:1636(C=N)，1510，1466，1438 (C = C)，1251(C－O)，1171，1045，603，535(S－O，S = O)cm^{-1}; Anal．calcd for C10H12 NO5 SK: C 40.36，H4.03，

N 4.69，S 12.11；found C 40.32，H 3.91，N 4.86， S 11.95。

Synthesis of complex1

In the reaction bottle, methanol (10 mL), water (20mL), $ZnCl_2$ (0.183g, 1mmol) and TISB 0.148 g (0.5mmol) are added successively to be dissolved. The reaction is about 2 h at normal temperature. Slowly add phen (0.198 g, 1 mmol) and DMF a few drops, drop, reflux reaction (60 °C), 5 h. Cool to room temperature, filter, filtrate at room temperature, slowly volatile, a few days later, brown black crystal of complex 1. IR ν: 3405(O—H)，1613(C = N)，1518，1464，1430 (C =C)，1210(C—O)，1159，1042，619，527(S—O ，S = O) cm^{-1}； Anal．calcd for C34 H37 N5O10 SZn: C 53.25，H 4.81，N 9.15，S 4.20; found C 53.06，H 5.08， N 9.35，S 9.68.

Structure determination

A suitable single crystal of complex**1** (0.36mm × 0.24mm × 0.11mm) was selected and glued on the tip of a glass fiber. The crystal structure was determined at 298K on an X-ray diffractometer, a Rigaku Xtalab detector diffractometer by using a Cu*Kα* radiation (λ = 0.154Å). All structures were solved using direct methods with SHELXS and refined by full-matrix leastsquares on *F*2 using the SHELXL14 software within OLEX2. All the non-hydrogen atoms were refined anisotropically with displacement parameters. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement using a riding model. Crystal data and structure parameters for the title complex are listed in Table 1.

Table 1 Crystal data for Zinc(II) Compound

Polymers	Complex1
Formula	C34 H37 N5 O10 SZn
Formula weight	772.63
Temperature(K)	298
Wavelength(A)	0.154
Crystal sizes(mm)	0.16mm × 0.24mm × 0.17mm
Color	colorless
Crystal system	monoclinic
Spaces group	C2 /c
a(A)	20.254 (1)
b(A)	16.128(1)
c(A)	12.657(3)
α(°)	102.561(4)
β(°)	98.372(5)
γ(°)	118.244(2)
Z	4

Table 2 elected Bonds Lengths (nm) and Bonds Angles(°)

Bond Lengths		Bond Angles			
Zn1-O1	1.862(1)	O1-Zn1-N2	90.92(1)	O1-Zn1-N4	83.42(5)
Zn1-N2	1.959(4)	O1-Zn1-N3	171.69(5)	N3-Zn1-N4	91.79(5)
Zn1-N5	1.891(7)	O1-Zn1-N1	90.64(2)	N2-Zn1-N5	174.82(1)
Zn1-N3	1.986(3)	N3-Zn1-N1	94.05(6)	N5-Zn1-N3	94.21(1)
Zn1-N1	1.994(6)	N5-Zn1-N4	82.13(2)	N5-Zn1-N1	92.64(3)
Zn1-N4	1.897 (5)	O1-Zn1-N5	83.74(2)	N2-Zn1-N4	92.37(1)
		N2- Zn1-N3	81.21(8)	N1-Zn1-N4	175.25(7)
		N2- Zn1-N1	83.77(4)		

Symmetry transformations used to generate equivalent atoms: #1: x, y, z

Results and Discussion

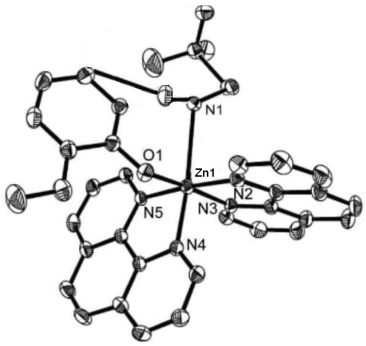

Fig.1 Crystal Structure of complex1

The center Zn (II) of complexes 1 with two phen molecules, respectively, coordinates with four N atoms. A N atom on the C=N double bond on the TISB, the O atoms of deprotonated phenolic hydroxyl coordinate to form six coordinated deformation of the octahedron. Among them, N (1) and N (4) are in the axial position, N (2), N (3), N (5) and O (1) are in the equatorial plane.

The bond angles formed with the central N(2) –Zn1 –N(3) is 81.21 (8) degrees. The bond angles formed with the central N (3) – Zn1–N (5) is equal to 94.21 (1) degrees. The bond angles formed with the central N (5) – Zn1–O (1) is about 83.74. (2) degrees. The bond angles formed with the central O (1) – Zn1– N (2) is 90.92 (1). The sum of the key angles is close to 360 degrees (350.08 degree), and the center Zinc (II) is separated from the plane N (2), /N (3), /N (5), /O (1) to 0.127nm. From the bond length data, it is known that the Zn1-N which is in the moleculer of phen, bond grows between 1.862 and 1.994, and is similar to other Zinc phenanthroline complexes. The determination of the dihedral angle between the two phen molecular plane is 81.93 degrees.

Among the complexes 1, there are two kinds of π-π stacking action between the rings of phen and the benzene ring of the TISB ligand, and the corresponding distances of their π-π stacking are 3.5167 and 3.5476 respectively. Although the sulfonate in the TISB ligand does not participate in the coordination of metal ions, it stabilizes complexes 1, it is through these two kinds of PI stacking action and hydrogen bonding to form a three-dimensional structure. Complexes 1 of the structure by hydrogen bonds formed with water molecules. In complexes 1, it is through these two kinds of PI stacking action and hydrogen bonding to form a three-dimensional structure.

IR Analysis

The infrared spectra of ligands and coordination polymers were determined by the potassium bromide tabletting method in the range of 4000 - 400cm^{-1} wavenumbers. There are strong peaks which were found near the 1613 cm^{-1}. It indicates the formation of C=N Schiff base. The absorption peaks of 162，1038，624 and 524 cm^{-1} are characteristic absorption peaks of sulfonic group. We also find absorption peaks at 1210 cm^{-1} which belong to C - O of phenol oxygen. The absorption peak at 1518，1464，1430 cm^{-1} belongs to the benzene. It is obviously that -OH stretching frequency of water molecules coordinate because of the presence of the broad band around 3405 cm^{-1}. Comparison with the infrared spectra of the ligand and the synthesized Zinc complex, it makes clear that the coordination bonds have formed.

Thermal Stability Behavior

The thermal decomposition curves of the complexes were measured at temperatures of 25-450℃. The thermal decomposition of the complex is divided into two parts. The first weightlessness process ranges from 25-250℃ to 0.598%, and the weight loss rate of the complexes is lost. The weight loss rate of the complexes between second weight loss processes at 250-450 ℃ is 29.288%, which is the decomposition of Schiff base complexes. The final residual rate was

70.114% for Zn-O and some residual groups for Schiff base

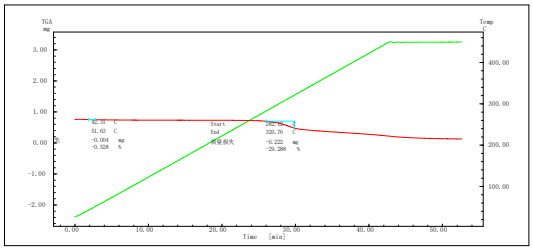

Fig.2 The thermogravimetric analysis of the complex1

Fluorescence properties

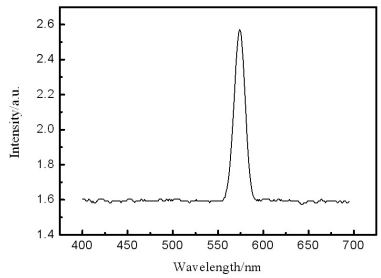

Fig.3 Fluorescence properties of complex1(Emission:575nm)

The fluorescence luminescence photometer was used to display the spectral range of 400nm~700nm The fluorescence spectra of the complex 1 are shown in Fig. 3. As shown as in Fig. 3, the emission wavelength of the complex 1 is about at 575nm. As we can see from Fig. 3, the wave crest has a pronounced blue shift (moving about 5nm to the left), indicating that the ligand affects the emission wavelength of Zn^{2+}. In addition, the height of the peak is higher than the fluorescence intensity of Zn^{2+} according to the relevant literature, indicating that the ligand sensitized the fluorescence of metal ions.

Conclusions

In this paper, we have presented the Zinc(II) complex $[Zn(TISB)(phen)_2]$ (TISB = the Schiff base synthesized by Isovanillin and taurine).The crystal structure of the Zinc (II) complex has been determined and studied by X-ray diffraction, which is also characterized by elemental analysis, IR spectra, thermogravimetric analysis. Fluorescence properties also have been studied in order to investigate the thermol behavior carefully.

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