

Syntheses, Crystal Structure and Fluorescence Property of Copper (II) Complex Constructed from 5-Sulfosalicylic Acid

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Abstract: The copper(II) complex[Cu(H₃ssal)(2,2'-bipy)(4,4'-bipy)(H₂O)](H₃ssal=5-sulfosalicylic acid) as synthesized with 5-sulfosalicylic acid by high pressure hydrothermal method. The crystal structure of the copper (II) complex contained derivative bipyridine ligands has been determined and studied by X-ray diffraction. Its structure was also characterized by elemental analysis, IR spectra. The copper(II) coordination units are connected, forming stereo structure. At the meanwhile, the luminescence properties are determined, which is shown the applications as photoactive materials.

Introduction

Over the past decades, the design and synthesis of metal-organic frameworks (MOFs), which is based on the selection of ligands and metal ions has already become a very interesting research field[1,2]. It is clear that the research of transition metal coordination polymers (CPs) is one of the most important fields in the study of coordination polymers. Therefore, research groups have paid close attention to not only the design and construction of the fascinating architectures coordination polymers, but also the properties and potential applications in the areas of luminescence, gas storage separation, conductivity, sensing, chirality, nonlinear optics, heterogeneous catalysis, magnetism, and molecular recognition. Among the achievements which have been reported, organic ligands with both carboxylate and sulfonate groups are especially fascinating, because they can adopt a variety of coordination modes and result in diverse multidimensional architectures. As a result of the transition metal coordination polymers not only show a rich and interesting structure of the topology, but also in the hole material, light and magnetic aspects of the unique nature still attracted great interest[3-5].

Pyridine, a kind of nitrogen containing heterocyclic compounds, is quite important in building MOFs, which also play a special magnetic activity effect. Pyridine has similar structures and properties with the introduction of benzene. Ligands which are containing pyridine ring to produce electronic coupling, often can significantly improve the luminescence properties of metal-organic frameworks. In this paper, in order to the synthesis of copper(II) and 5-sulfosalicylate compounds with chelating ligands, we choose pyridine which contains different heterocyclic N atoms, such as 2, 2'-bipy and 4,4'- bipy. We also have investigated the configuration activity of their diverse structural

topologies, the thermal properties, and the luminescence properties.

Experimental Details

General Comments

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. A crystal suitable for X-ray determination was mounted on a glass fiber. All data were collected at room temperature on a Rigaku XtaLAB imaging plate area detector with graphite monochromated Mo-K α radiation ($\lambda = 0.71073\text{\AA}$). Elemental analyses for Carbon(C), hydrogen(H) and nitrogen(N) were carried out on a FLASH EA1112 elemental analyzer. Fourier transform infrared (FT-IR) spectra were carried out on Shimizu IRAffinity-1 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. Shimizu TGA-50 is applied for measuring the thermal properties. The photoluminescence study was carried out on powdered sample in the solid state using Gangdong spectrometer at room temperature.

Synthesis of the copper complex [Cu(H₃ssal)(2,2'-bipy) (4,4'-bipy)(H₂O)]

A mixture of Cu(CH₃COO)₂•H₂O (0.199g, 1.0 mmol), 5-sulfosalicylic acid dihydrate (0.254 g, 1.0 mmol), 2,2'-bipy (0.156 g, 1.0 mmol), and 4,4'-bipy (0.156 g, 0.49 mmol) in a water/ethanol (1:1) solution (20 mL) were added to 25mL Teflon-lined autoclave reactor after stirring for 30 min for the sake of sufficient dispersion. A light blue solid was quickly precipitated without further filtration. The Teflon-lined autoclave was sealed into stainless steel and heated at 140 °C for 48 h, which was then cooled down to room temperature at a rate of 10 °C/h. Blue block-shaped crystals were obtained in another 1 week. Yield: 52% based on a copper salt. Anal Calcd for C₂₇H₂₀N₄O₆CuS: C, 57.85; H, 3.57; N, 9.99. Found: 57.81, 3.54, 9.98. IR (KBr pellet, cm^{-1}): 3607(m), 3450(m), 1589(s), 1572(m), 1486(m), 1477(w), 1445(m), 1424(s), 1385(w), 1379(w), 1316(w), 1304(w), 1209(s), 1171(s), 1128(m), 1085(w), 1047(s), 1012(m), 897(w), 821(m), 770(w), 756(w), 734(w), 678(m), 646(w), 604(m), 582(m), 540(w), 453(w), 417(w), 412(w).

Structural Determinations

The structures were solved by direct methods and expanded with Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. All calculations were performed using the SHELXL-97 crystallographic software package[6]. Details of the X-ray experiments and crystal data of the compound are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

Table 1 Crystal data for copper(II) Compound

Polymers	data
Formula	C ₂₇ H ₂₀ N ₄ O ₆ CuS
Formula weight	560.19
Temperature(K)	413(2)
Wavelength(A)	0.71073
Crystal sizes(mm)	0.14×0.18×0.23
Color	blue
Crystal system	triclinic
Spaces group	P-1
a(A)	9.356 (1)
b(A)	17.962(2)
c(A)	13.437(8)

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

Bond Lengths		Bond Angles	
Cu1-O1 ⁱ 2.325(1)	O1 ⁱ -Cu1-O2 ⁱ 54.16(12)	O1 ⁱ -Cu1-O4 88.62(13)	
Cu1-O2 ⁱ 2.265(4)	O1 ⁱ -Cu1-N1 75.98(14)	O1 ⁱ -Cu1-N2 122.73(14)	
Cu1-O4 2.591(7)	O2 ⁱ -Cu1-O4 139.56(13)	O2 ⁱ -Cu1-O5 ^{II} 91.81(13)	
Cu1-O7 3.057(3)	O2 ⁱ -Cu1-N2 81.67(14)	O2 ⁱ -Cu1-N1 84.28(15)	
Cu1-N1 2.481(6)	O4-Cu1-O6 ^{II} 81.83(12)	O4-Cu1-N1 74.60(14)	
Cu1-N2 2.601 (5)	O4-Cu1-N2 118.54(14)	N1-Cu1-N2 62.89(15)	

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

Results and Discussion

Structural Description

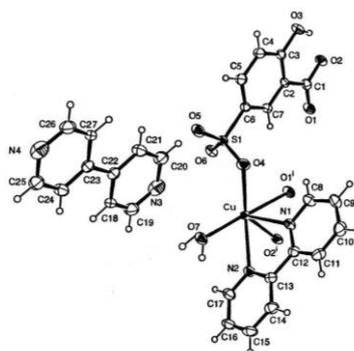


Fig.1 Crystal Structure of [Cu(H₃ssal)(2,2'-bipy)(4,4'-bipy)(H₂O)]

Considering the copper(II) complexes in coordination modes and structural topologies gives rise to some valuable information. As shown in Figure 1, the ordination environment of each Cu(II) atom consists of two nitrogen atoms of one 2,2'-bipy, three carboxylate oxygen atom of one H₃ssal ligand, and one oxygen atom from one water molecule, while the 4,4'-bipy ligand only acts as a guest molecule in the crystal packing. As shown in Table 2, the O7 atom from the water molecule is located in the apical position with a 3.507(3) Å distance, which is longer than other five bonds obviously. In addition, it has been observed that Cu-N bond lengths fall in the range of 2.42-2.60 Å for complex, that Cu-N distances fall well within the ranges usually observed in copper(II) complexes containing the bipyridine ligands.

IR Analysis

Comparison with the infrared spectra of the ligand H₃ssal and the synthesized copper complex, there are no strong peaks which were found near the 1680 cm⁻¹, indicating that the proton of the both -COOH and -SO₃H of the 5-sulfosalicylic acid has been removed from these compounds. It is obviously that -OH stretching frequency of water molecules coordinate because of the presence of the broad band around 3430 cm⁻¹. The asymmetric stretching vibration peaks of the complex is present around 1589 and 1572 cm⁻¹, while the symmetric stretching vibration peaks of the carboxyl groups were in the range of 1379, 1385, 1424 and 1445 cm⁻¹, respectively. The characteristic vibrations of asymmetric stretching vibration peaks of the complex are observed at 1209, 1171, and 1128 cm⁻¹.

Thermal Stability Behavior.

In order to discuss the thermal stability of the title complex, the thermogravimetric analysis of the

copper complex is carried out under conditions of temperature with the increasing rate $10^{\circ}\text{C}/\text{min}$, from 20°C to 450°C . Thermal analysis of complex shows that the weight loss starts at 151°C of the range $151\text{-}183^{\circ}\text{C}$, the total loss of 27.52% attributed to the release of 4,4'-bipy (calculated 27.85%). The exquisite weight loss appears at $223\text{-}248^{\circ}\text{C}$, which is corresponding to the organic ligand. The final residues is comparing with other complexes which are depending on the bridging ligands, the network structure constructing with chelating ligands is relatively unstable.

Luminescence Properties

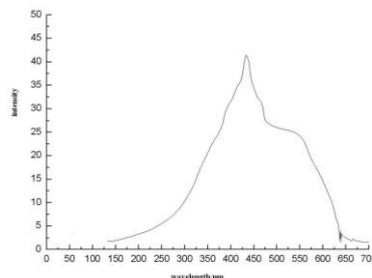


Fig.2 Emission spectra of the title complex

The transition metals of d^{10} are well-known for the photoluminescence properties. As shown in Fig2, there is an intense fluorescent emission of complex at 452.3 nm that was observed in the solid state at room temperature. In comparison to the 5-sulfosalicylic acid ligand whose peaks appear at 414 nm, the red-shifted is nearly 40 nm. Peaks of complexes are lower than those in ligand. Such fluorescent properties are attributed to the result of coordination action between copper and the ligands containing 2,2'-bipyridine and 5-sulfosalicylic acid ligands. Therefore, the synthesized complex maybe has the potentials that can be used to prepare some photoactive materials.

Conclusions

In this paper, we have presented the copper(II) complex $[\text{Cu}(\text{H}_3\text{ssal})(2,2'\text{-bipy})(4,4'\text{-bipy})(\text{H}_2\text{O})]$ (H_3ssal = 5-sulfosalicylic acid) with 5-sulfosalicylic acid, 2,2'-bipy and 4,4'-bipy. The crystal structure of the copper (II) complex has been determined and studied by X-ray diffraction, which is also characterized by elemental analysis, IR spectra. The Copper(II) coordination units shows novel stereo structure. Fluorescent properties of complex indicate interesting potential applications in photoactive materials.

Acknowledgements

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