Journal of Molecular Structure 1112 (2016) 147–154

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Synthesis and photoluminescence properties of silver(I) complexes based on *N*-benzoyl-L-glutamic acid and *N*-donor ligands with different flexibility

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A R T I C L E I N F O

Article history:
Received 4 December 2015
Received in revised form
27 January 2016
Accepted 27 January 2016
Available online 5 February 2016

Keywords:
Crystal structure
N-Benzoyl-L-glutamic acid
N-donor ligands
Photoluminescent properties
Solid-state circular dichroism spectra

A B S T R A C T

By changing the *N*-donor ancillary ligand, three novel silver (I) complexes $\{[Ag(HbzgluO)(4,4'\text{-bipy})]\cdot H_2O\}_n$ (**1**), $\{[Ag_2(HbzgluO)_2(bpe)_2]\cdot 2H_2O\}_n$ (**2**) and $\{[Ag(HbzgluO)(bpp)]\cdot 2H_2O\}_n$ (**3**) ($H_2bzgluO$ = *N*-benzoyl-L-glutamic acid, 4,4′-bipy = 4,4′-bipyridine, bpe = 1,2-di(4-pyridyl)ethane, bpp = 1,3-di(4-pyridyl)propane) were synthesized. Their structures have been determined by single-crystal X-ray diffraction analyses and further characterized by elemental analyses, IR spectra, powder X-ray diffraction (PXRD), and thermogravimetric analyses (TGA). In this study, the *N*-donor ligands are changed from rigidity (4,4′-bipy), quasi-flexibility (bpe) to flexibility (bpp), the structures of complexes also change. Complex **1** features a 1D chain structure which is further linked together to construct a 2D supramolecular structure through hydrogen bonds. Complex **2** is a 1D double-chains configuration which eventually forms a 3D supramolecular network via hydrogen bonding interactions. Whereas, complex **3** exhibits a 2D pleated grid structure which is linked by hydrogen bonding interactions into a 3D supramolecular network. The present observations demonstrate that the modulation of coordination polymers with different structures can accomplish by changing the spacer length of *N*-donor ligands. In addition, the solid-state circular dichroism (CD) spectra indicated that compound **2** exhibited negative cotton effect which originated from the chiral ligands $H_2bzgluO$ and the solid-state fluorescence spectra of the three complexes demonstrated the auxiliary ligands have influence on the photoluminescence properties of the complexes.

1. Introduction

Over the past decades, considerable efforts have been devoted to the theoretical prediction and the control of structures of chiral metal-organic coordination compounds not only for their fascinating structural architectures but also for chiral separation, asymmetric catalysis, luminescence, magnetism, and nonlinear optical applications [1–8]. The syntheses of chiral coordination frameworks have been accomplished in the following two ways. One option is to use chiral organic ligand as linker to connect metal centers or metal clusters. The other option is to employ achiral ligand via spontaneous resolution on crystallization without any chiral auxiliary. The most direct route is using the chiral ligands to prepare the chiral coordination polymers [9–12]. However, the formations of desirable complexes are also sensitive to many complicated factors such as the solvent system, the assistant ligands and the reaction temperature [13–16]. So it is still a great challenge to predict the structures and properties of the target coordination polymers [17–21].

To the best of our knowledge, chiral amino acid derivatives have widespread availability, multiple metal binding sites, and versatile bonding modes, so they can be ideal candidates for assembling compounds [22–24]. Through observation, we found that the *N*-benzoyl-L-glutamic acid [25,26] as a very flexible chiral ligand, which possesses several interesting characteristics. On the one hand, it has two carboxyl groups that may be partially or completely deprotonated, inducing rich-coordination modes and allowing higher dimensionality. On the other hand, it can act either as a hydrogen-bond acceptor or donor, depending upon the degree of deprotonation. These characters may lead to the novel motifs with unique structures. Moreover, the complexes based on *N*-benzoyl-L-glutamic acid have rarely been documented to date [27].

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http://dx.doi.org/10.1016/j.molstruc.2016.01.077

In the present communication, we have reported two chiral zinc coordination polymers based on H_2bzgluO, {[Zn(bzgluO)(bpp)]·1.75H_2O}$_n$ and [Zn(bzgluO) (4,4-bipy)$_{0.5}$]$_n$. In order to further study that the effect of different transition metals and N-donor ancillary ligands, we keep on the following work.

We find the ancillary *N*-donor ligands also play an important role in the design and construction of various coordination polymers [28–30]. So we research the effect of the ancillary *N*-donor ligands on the assembly and structures of target complexes. Three different *N*-donor ancillary ligands (4,4′-bipy, bpe and bpp) with different flexibility [31–33], were selected for constructing coordination polymers.

Ag(I) ion with d^{10} closed-shell electronic configuration exhibits articular photoluminescent property and adopts a variety of coordination number leading to diverse coordination geometries (linear, trigonal, and tetrahedral coordination geometry) [34–36]. In addition, Ag(I) ion is apt to form Ag·Ag, Ag&middotπ, and Ag&middotS contacts, which help to improve the related properties in the studies of optoelectronic materials [37].

With this background information, we sought to investigate the role of the *N*-donor ancillary ligands with different flexibility in the structural diversity of Ag (I) coordination polymers. Herein, we reported the syntheses and characterizations of three novel coordination polymers: {[Ag(HbzgluO) (4,4′-bipy)]•H_2O}$_n$ (**1**), {[Ag_2(HbzgluO)$_2$ (bpe)$_2$]·2H_2O}$_n$ (**2**) and {[Ag(HbzgluO)(bpp)]·2H_2O}$_n$ (**3**), which features 1D chain, 1D double-chain and 2D pleated grid structure, respectively. This result reveals that the formation of complexes with different structures are well-controlled by modulating the spacer length of *N*-donor ligands, which may provide us with a simple and efficient synthetic route for the tunable construction of complexes. Meanwhile, complex **2** exhibits obvious negative cotton effect which originated from the chiral ligands H_2bzgluO in the solid state. Luminescent properties of complexes **1**–**3** have been examined in solid states at room temperature.

2. Experimental

2.1. General characterization and physical measurements

All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. Infrared (IR) spectra were recorded using KBr pellets from 4000 cm^{-1}–400 cm^{-1} on a Fourier-transform infrared-8900 spectrometer. Elemental analyses (C, H and N) were performed on a Vario EL analyzer. Thermogravimetric analyses (TGA) were carried out on a simultaneous STA 499 F3 thermal analyzer under nitrogen with a heating rate of 10 °C min^{-1} from room temperature to 850 °C. The solid state circular dichroism (CD) spectra were recorded on a JASCOJ-810 spectropolarimeter with KCl pellets. Fluorescence spectra were recorded on a Hitachi F-4500 luminescence spectrometer.

2.2. Preparations

2.2.1. Synthesis of {[Ag(HbzgluO) (4,4′-bipy)] H_2O}$_n$ (**1**)

An ethanol (8 ml) containing 4,4′-bipy (15.6 mg, 0.1 mmol) was slowly added to a solution of H_2bzgluO (25.1 mg, 0.1 mmol), $AgNO_3$ (17.0 mg, 0.1 mmol) and NaOH (4.0 mg, 0.1 mmol) in aqueous solution (8 ml). The mixture was stirred for 10 min at room temperature and then filtered. The filtrate was left to stand at room temperature for six days and so to deposit colorless crystals of complex **1**. The colorless crystals obtained were suitable for X-ray analysis with 56% yield based on Ag. Anal. Calcd. for {[Ag(HbzgluO) (4,4′-bipy)] H_2O}$_n$ $C_{22}H_{21}AgN_3O_6$(%). C, 49.64; N, 7.89; H, 4.17. Found: C, 49.62; N, 7.97; H, 4.25. IR (KBr, cm^{-1}) ν: 3408(b), 3385(m), 3066(w), 2360(w), 1734(w), 1647(s), 1600(s), 1560(s), 1521(s), 1487(m), 1410(m), 1388(w), 1319(w), 1259(w), 1201(w), 1068(w), 891(w), 806(s), 717(w), 689(w), 626(w), 635(s), 472(s).

2.2.2. Synthesis of {[Ag_2(HbzgluO)$_2$(bpe)$_2$]·2H_2O}$_n$ (2)

This compound was synthesized in a procedure analogous to that of **1** except that bpe was used instead of 4,4′-bipy and methanol was took the place of ethanol. The colorless crystals of complex **2** obtained were suitable for X-ray analysis with 36% Yield based on Ag. Anal. Calcd. for {[Ag_2(HbzgluO)$_2$ (bpe)$_2$]·2H_2O}$_n$ $C_{24}H_{28}AgN_3O_7$(%). C, 49.79; N, 7.26; H, 4.84. Found: C, 49.64; N, 7.64; H, 4.83. IR (KBr, cm^{-1}) ν: 3407(b), 3068(w), 2935(w), 1696(w), 1647(m), 1605(s), 1580(m), 1474(w), 1399(s), 1217(w), 1077(w), 1010(w), 820(s), 713(s), 548(w).

2.2.3. Synthesis of {[Ag(HbzgluO)(bpp)]·2H_2O}$_n$ (3)

$AgNO_3$ (17.0 mg, 0.1 mmol), H_2bzgluO (25.1 mg, 0.1 mmol) and bpp (19.8 mg, 0.1 mmol) in H_2O(10.0 mL) were mixed in a 23 mL Teflon reactor, which was then heated to 120 °C for 5 days. The resulting solution was left to cool slowly to room temperature. colorless crystals of compound **3** suitable for X-ray determination were obtained in 61% yield based on Ag. Anal. Calcd. for {[Ag(HbzgluO)(bpp)]·2H_2O}$_n$ $C_{25}H_{30}AgN_3O_7$(%). C, 50.69; N, 7.09; H, 5.10. Found: C, 50.85; N, 7.03; H, 5.04. IR (KBr, cm^{-1}) ν: 3398(s), 3385(s), 3064(s), 2941(w), 2860(w), 2314(w), 1647(s), 1604(s), 1577(s), 1541(s), 1419(m), 1396(m), 1220(w), 1099(w), 1068(w), 1012(w), 808(m), 715(m), 601(w), 513(w).

2.3. X-ray crystallography

X-ray single crystal data of the compounds **1**–**3** were collected on a Bruker SMART diffractometer equipped with CCD area detector with a graphite monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo–Kα radiation (λ = 0.71073 Å) at 298(2) K by *φ*-*ω* scan mode. All data were corrected by semi-empirical method using SADABS program. The program SAINT was used for integration of the diffraction profiles. All structures were solved by direct methods using SHELXS program of the SHELXTL-97 package and refined with SHELXL-97 [38]. Metal atom centers were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinements were performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. All the hydrogen atoms were first found in difference electron density maps, and then placed in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded. Details of the data collection and refinement for complexes **1**–**3** are given in Table 1, and the selected bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. Structural description of the title complexes

3.1.1. {[Ag(HbzgluO) (4,4′-bipy)] H_2O}$_n$ (**1**)

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the triclinic space group P$\bar{1}$, which is a 1D infinite single-chain. In the asymmetric unit of **1**, there is one crystallographically independent Ag(I) ion, one 4,4′-bipy ligand, one HbzgluO$^-$ anion, and one lattice water molecule, as shown in Fig. 1a. The central Ag(I) ion exhibits triangle coordination geometry defined by two nitrogen atoms (N1, N2) from two 4,4′-bipy