Journal of Molecular Structure 1155 (2018) 303–309

Contents lists available at ScienceDirect

Journal of Molecular Structure

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

Structural diversity of three Cu(II) compounds based on a new tripodal zwitterionic ligand: Syntheses, structures and properties

Jie Zhou, Jing-Song Zhao, Jing Feng, Xiao-Feng Zhang, Jian Xu, Lin Du, Ming-Jin Xie, Qi-Hua Zhao*

Key Laboratory of Medicinal Chemistry for Natural Resource Education Ministry, School of Chemical Science and Technology, Yunnan University, Kunming, 650091, PR China

ARTICLE INFO

Article history:
Received 28 July 2017
Received in revised form
15 October 2017
Accepted 27 October 2017
Available online 28 October 2017

Keywords:
Copper complex
Crystal structure
Photoluminescence property
pH dependent
Magnetic property
Zwitterionic ligand

ABSTRACT

An exploration of reactions of 1,1′,1″-(benzene-1,3,5-triyltris(methylene))tris(4-carboxypyridinium)-tribromide (H_3LBr_3) with Cu(II) salt under different pH conditions has led to the formation of three complexes, $[Cu(HL)_2(H_2O)_3]\cdot4(ClO_4)\cdot3H_2O$ (**1**), $[Cu_2(HL)(\mu_3\text{-}OH)(\mu_2\text{-}H_2O)(H_2O)_2]\cdot4(ClO_4)\cdot6H_2O$ (**2**), and $[Cu_3(L)_2Cl_6(H_2O)_4]\cdot4H_2O$ (**3**). Single-crystal X-ray analyses revealed that complex **1** displays a discrete mononuclear structure with the ligand in a bowl-shaped configuration. Complex **2** possesses a tetranuclear 1D beaded chain structure. While complex **3** features a discrete trinuclear 'H-type' structure with the ligand in a chair-like configuration. The distinct compositions and structures of **1**–**3** are mainly ascribed to the different pH values of the reaction solution, the influences of anions, as well as the configurations which the zwitterion ligands adopt. The magnetic properties of **2**, and the photoluminescence properties of **2**, and **3** have been investigated. Moreover, powder X-ray diffraction, infrared spectroscopy, and elemental analysis were also performed.

1. Introduction

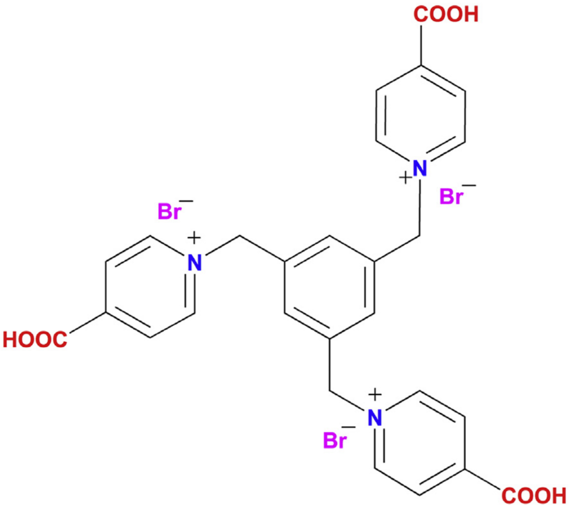
Over the past years, due to their rich and varied structures as well as interesting properties, rational design and assembly of coordination polymers (CPs) with predictable structures and desirable properties has attracted sustained attentions [1–3]. So far, many efforts have been made and a lot of structurally intriguing CPs with valuable properties have been synthesized [4–7], however, design and synthesis of CPs with desired structure in a truly rational manner is still difficult for chemists [8–10]. From the view of synthetic strategy, the structure and functionality of these hybrids significantly depends on the selection of appropriate organic ligands [11] and metal centers [12], as well as the reaction conditions such as temperature [13], pH value [14], solvent [15], ligand-configuration [16], and guest molecules [17]. In recent years, zwitterionic (ZW) carboxylate ligands have become promising building blocks in the design and synthesis of CPs owing to their ready availability and flexible coordination abilities and configurations [18–22]. Compared with the usual carboxylate ligands, the chemistry of ZW carboxylate ligands have been studied limitedly so far.

Taking all of the observations into consideration, the ZW ligand, 1,1′,1″-(benzene-1,3,5-triyltris(methylene))tris(4-carboxypyridinium)-tribromide (H_3LBr_3) (Scheme 1), with three positively charged pyridinium units and three negatively charged bromide anions, is introduced here. Because of the flexible tethers between the pyridinium-carboxylate moieties, the tricarboxylate ligand may adopt two different conformations (*cis*-, and *trans*-), which is similar to the previously reported tripodal zwitterionic ones [23–27]. Complex constructed by H_3LBr_3 is still limited [28]. In this paper, H_3LBr_3 was chosen to react with Cu(II) salt under different pH conditions. Three structurally interesting copper complexes; $[Cu(HL)_2(H_2O)_3]\cdot4(ClO_4)\cdot3H_2O$ (**1**), $[Cu_2(HL)(\mu_3\text{-}OH)(\mu_2\text{-}H_2O)(H_2O)_2]\cdot4(ClO_4)\cdot6H_2O$ (**2**), and $[Cu_3(L)_2Cl_6(H_2O)_4]\cdot4H_2O$ (**3**) were obtained. The complexes were characterized by X-ray crystallography, IR, elemental analyses, and powder X-ray diffraction analyses. Moreover, magnetic properties of **2**, and luminescent properties of **2** and **3** were also investigated.

---

* Corresponding author.
E-mail address: qhzhao@ynu.edu.cn (Q.-H. Zhao).

https://doi.org/10.1016/j.molstruc.2017.10.100
0022-2860/



Scheme 1. The structure of H_3LBr_3 ligand.

2. Experimental

2.1. Physical measurements

All analytical-grade chemicals and solvents were commercially available and used as received without further purification. Elemental analyses for C, H, and N were carried out with an Elementar Vario ELIII analyzer. Fourier-transform (FT) infrared (IR) spectra were recorded as KBr disks on an FTS-40 IR infrared Spectrometer in the 4000–400 cm^{-1} region. The phase purity of the samples was investigated by powder X-ray diffraction (PXRD) measurements carried out on a Bruker D8-Advance diffractometer equipped with Cu-Kα radiation ($\lambda = 1.5418$ Å) at a scan speed of 1°/min. Simulation of the PXRD patterns were performed using single-crystal data and processed with the Mercury 3.9 program available free of charge through the Internet at http://www.iucr.org. Solid-state fluorescence spectra were measured at room temperature on a Hitachi FL-7000 fluorescence spectrophotometer with excitation and emission slit widths of 5 nm. Variable-temperature susceptibility measurements of crystalline samples were performed on a Quantum Design MPMS-XL SQUID magnetometer. Diamagnetic corrections were performed from Pascal's constants, and an experimental correction for a sample holder was also applied.

2.2. Synthesis of H_3LBr_3 and the complexes

2.2.1. Synthesis of H_3LBr_3

The zwitterion H_3LBr_3 ligand was synthesized according to the route as shown in Scheme S1. A mixture of 1,3,5-tris(bromomethyl)-benzene (6.0 g, 15 mmol) and ethyl isonicotinate (6.8 g, 45 mmol) in 80 mL of CH_3CN was refluxed for 3 days. After the mixture was cooled down to room temperature, the resulting yellow precipitate was filtered, washed with CH_3CN, and dried at room temperature to give the ester of L. The resultant was dissolved in 20% HCl (w/w; 80 mL) and was subsequently refluxed for 12 h. The solvent was removed under reduced pressure to give a white power. (Yield: 8.9 g, 87.6%). Anal. Calc. for $C_{27}H_{24}Br_3N_3O_6$(%): C 44.66; H 3.33; N 5.79. Found: C 44.95; H 3.61; N 5.48.

2.2.2. Synthesis of $[Cu(HL)_2(H_2O)_3]\cdot4(ClO_4)\cdot3H_2O$ (**1**)

H_3LBr_3 (0.0726 g, 0.1 mmol) was dissolved in distilled water (3.5 mL), and the pH value of the solution was adjusted to 5 with NaOH (0.1 mol/L). Then $Cu(ClO_4)_2\cdot6H_2O$ (0.1112 g, 0.3 mmol) was added to this solution. The mixture was stirred for 10 min at ambient temperature and then filtered. The clear blue filtrate was kept in the dark and was slowly evaporated at room temperature. A few weeks later, green crystals suitable for X-ray analysis were obtained. Yield: 0.157 g, 33.9%. Elemental Anal. Calc. for $C_{54}H_{56}Cl_4CuN_6O_{34}$: C, 42.16; H, 3.67; N, 5.46. Found: C, 42.81; H, 3.93; N, 5.74. IR (KBr pellet, ν/cm^{-1}): 3420(br), 3123(w), 2022(w), 1613 (vs), 1563(s), 1398(vs), 1088(vs), 778(m), 628(s).

2.2.3. Synthesis of $[Cu_2(HL)(\mu_3\text{-}OH)(\mu_2\text{-}H_2O)(H_2O)_2]\cdot4(ClO_4)\cdot6H_2O$ (**2**)

Complex **2** was synthesized similarly as **1**, except that the amount of $Cu(ClO_4)_2\cdot6H_2O$ was extended to 0.7 mmol (0.2594 g) and the pH value of the solution was adjusted to 8. A few weeks later, dark-green crystals suitable for X-ray analysis were obtained. Yield: 0.252 g, 60.6%. Elemental Anal. Calc. for $C_{27}H_{41}Cu_2N_3O_{20}Cl_4$: C, 27.29; H, 3.48; N,3.54. Found: C, 27.45; H, 3.60; N, 3.47. IR (KBr pellet, ν/cm^{-1}): 3466(s),1616 (vs), 1565(s), 1454(w), 1399(vs), 1088(vs), 873(w), 782(w), 626(w).

2.2.4. Synthesis of $[Cu_3(L)_2Cl_6(H_2O)_4]\cdot4H_2O$ (**3**)

Complex **3** was synthesized similarly as **1**, except that $Cu(ClO_4)_2\cdot6H_2O$ (0.1112 g, 0.3 mmol) was replaced with $CuCl_2\cdot2H_2O$ (0.0853 g, 0.5 mmol) and the pH value of the solution was adjusted to 10. A few weeks later, brown crystals suitable for X-ray analysis were obtained. Yield: 0.162 g, 64.2%. Elemental Anal. Calc. for $C_{27}H_{29}Cl_3Cu_{1.5}N_3O_{10}$: C, 42.83; H, 3.86; N, 5.55. Found: C, 42.36; H, 3.68; N, 5.30. IR (KBr pellet, ν/cm^{-1}): 3434(w), 3043(w), 1635 (vs), 1560(s), 1450(w), 1370 (vs), 1126(w), 881(w), 800(s), 702(w).

2.3. X-ray crystallographic measurements

The selected single crystal with suitable dimensions was mounted on a glass fiber and used for X-ray diffraction analyses. Crystallographic data were collected at 293 K on a Bruker Smart AXS CCD diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) using ω–scan technique. Structures were solved by direct methods, and non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELX-97 package [29–31]. Hydrogen atoms attached to the organic moieties were either located from the difference Fourier map or fixed stereochemically. From the difference Fourier map of **1** and **2**, a number of diffuse scattered peaks with electron density were observed, which can be attributed to four disordered ClO_4^- anions and a number of water solvent molecules. Attempts to model these peaks were unsuccessful because the residual electron density peaks obtained were diffused. So SQUEEZE was used to eliminate the disorder of the lattice solvents [32]. There is a SQUEEZE addition at the end of each CIF for complexes **1** and **2**. Check CIF/PLATON test generates some level B alerts for ‘D–H without acceptor’ and one ‘short non-bonding intra D–H···H–X contact’ with the refined structure, wherefore the acceptors are squeezed and some of water H-atoms should not be placed on the reported locations. Therefore, final chemical formula of the structures of **1** and **2** was set with the guest solvent molecules of crystallization. Details of the crystallographic data collection and refinement parameters are summarized in Table 1, selected bond distances and angles are given in Table S1.