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Syntheses, Structures, and Properties of Coordination Compounds with Aromatic Heterocyclic Ligands

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ABSTRACT Four coordination compounds $Pb(Hbtca)(phen)(NO_3)\cdot 1.63H_2O$ (**1**), $Pb(phen)_2(NO_3)_2$ (**2**) $Cu(2,2'\text{-bipy})Cl_2$ (**3**) $Co(4,4'\text{-bipy})_3(H_2O)_2$ (**4**) (H_2btca = 1H-1,2,3-benzotriazole-5-carboxylic acid, phen = 1,10-phenanthroline, 2,2′-bipy = 2,2′-bipyridine, and 4,4′-bipy = 4,4′-bipyridine) have been synthesized and structurally characterized. For compound **1**, each Pb atom is five-coordinated by two carboxylate oxygen atoms from one $Hbtca^{2-}$ anion, two nitrogen atoms from one phen molecule, and one nitrate oxygen atom. Hydrogen bonding plays a significant role in constructing one-dimensional supramolecular structure. The metal ions bind to the nitrogen-donor auxiliary ligands without the $Hbtca^{2-}$ ligands in compounds **2**–**4**. They feature mononuclear, dinuclear, and one-dimensional straight chain structures, respectively. Compound **1** exhibits broad the fluorescent emission band at 564 nm, which can be attributed to the charge transfer transitions between metal ions and ligands.

KEY WORDS Coordination compounds, Heterocyclic ligands, 1*H*-1,2,3-Benzotriazole-5-carboxylic acid, 2,2′-Bipyridine.

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INTRODUCTION

Recently, coordination compounds with diverse architectures and potential applications in single-molecule magnet, molecular sensing, photoluminescence, catalyst support, and adsorption, have already become an important aspect in the hybrid materials research.[1-5] They integrate the characteristics of metal ions and organic ligands, which provide an effective strategy for the design and acquisition of new hybrid materials.[6] In the rational design and syntheses, nitrogen heterocyclic ligands are usually used as building blocks for constructing interesting and intricate structures.[7-9] Fortunately, modified heterocyclic ligands with other functional groups, such as carboxylate, sulfonate, or phosphonate groups, usually were employed as building units for increasing coordination sites and rich coordination modes.[10,11] One novel coordination polymer $[Co_3(L)_2(H_2O)_2]_n\cdot nCH_3CN\cdot nH_2O$ (H_3L = 5-(2,3-dicarboxylphenoxy)nicotic acid) was solvothermally constructed by the N-heterocyclic carboxylate bifunctional ligand. It displays a 2D framework based on the $[Co_3(COO)_4]$ second building units with the point symbol of $(4^{18}\cdot 6^{10})(4^5\cdot 6)_2$.[12] One complex $[BaL(ClO_4)(H_2O)]_n$ was constructed from the 4-pyridinyl-pyrimidine-2-sulfonate (L^-). L^- ligand adopts μ_4-hexadentate coordination mode and forms a 3D network.[13] Frequently, introducing the auxiliary N-donor ligands to the metal centers are contributing to main ligands coordination with metal ions. Furthermore, the existence and changes of them have a great effect on the resulting structures.[14,15]

H_2btca is served as the heterocyclic ligand, which is very attractive because it provides an N1, N2 connection between two separated metal ions. Moreover, its functionalization with carboxylate group affords a wide range of possibilities to coordinate with metal centers and obtain coordination compounds with different architectures. Herein, a new coordination compound, $Pb(Hbtca)(phen)(NO_3)\cdot 1.63H_2O$,

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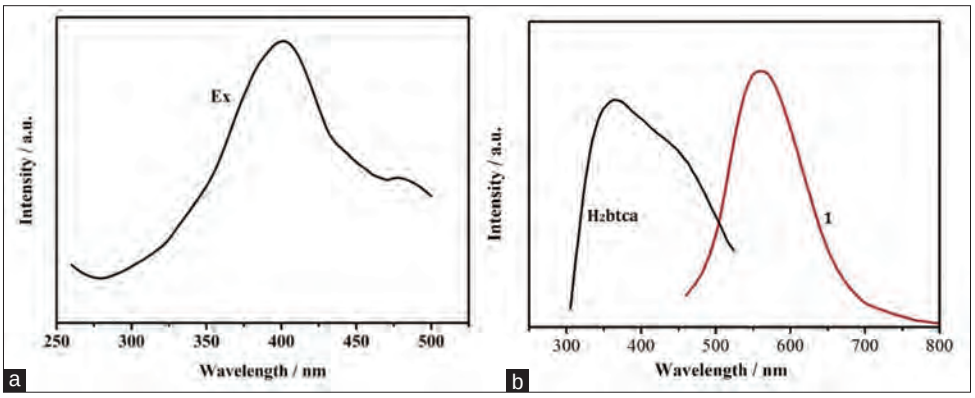

Figure 8: (a) Solid-state excitation spectrum of compound 1; (b) solid-state emission spectra of free H_2btca ligand and compound 1 at room temperature

after 9 days in the yield of 62% based on Cu. **Anal. Calced.** for $C_{10}H_8Cl_2N_2Cu$ (290.62): C41.33, H2.77, N9.64; found C41.37, H2.82, N9.66.

Synthesis of compound 4

The synthetic procedure for compound **4** was similar to that for compound **1**, but replacing $Pb(NO_3)_2$ and phen with $Co(NO_3)_2$ and 4,4′-bipy. Red blocked crystals of compound **4** were obtained with the yield of 52% based on 4,4′-bipy. **Anal. Calced.** for $C_{30}H_{26}N_6O_2Co$ (561.5): C64.17, H4.67, N14.97; found C64.20, H4.73, N14.98.

X-ray crystallographic measurement

Single crystal X-ray data for compounds **1–4** were collected with a Bruker Apex-II diffractometer, employing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The collected data were reduced using the SAINT program, and absorption corrections were applied to the data using the SADABS program. The structures were solved by the direct method and refined by the full-matrix least-squares method based on F_2, using SHELX-2014 software.[24,25] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were treated by independent and constrained refinements.

CONCLUSION

We reported the synthesis, crystal structure, and characterization of one new Pb coordination compound, $Pb(Hbtca)(phen)(NO_3)\cdot 1.63H_2O$, derived from $Hbtca^-$ ligand. The inter-molecular hydrogen-bonding interactions involved in compound **1** lead to the formation of one-dimensional chain structure. Structural study reveals that the structures of the compounds **2–4** are mainly determined by the hetero N-donor ligands. They feature mononuclear, Cl-bridged dinuclear, and one-dimensional chain structures with phen, 2,2′-bipy, and 4,4′-bipy, leaving the $Hbtca^-$ ligands without crystallization, respectively. Compound **1** exhibits broad fluorescent emission band at 564 nm in the solid state. The charge transfer of Pb ions to the ligands in compound **1** is responsible for the red-shifted behavior of 200 nm in contrast to H_2btca ligand.

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