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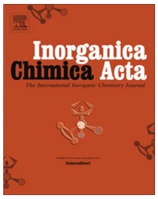

Research Paper

Influence of N-donor ancillary ligands on the structures of three cadmium(II) complexes with L-shaped carboxylate ligand

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ABSTRACT

This work presents a systematic investigation on reactions of cadmium nitrate with L-shaped 1-carboxymethylpyridinium-4-carboxylate (L) ligand in the presence of three different N-donor ancillary ligands 2,2′-bipyridine (2,2′-bipy), 1,10-phenanthroline (1,10-phen), and 4,4′-bipyridine (4,4′-bipy). Three new cadmium(II) complexes, namely, $[Cd(L)_2(H_2O)_4]$ (**1**), $[Cd(L)_2(1,10\text{-phen})]\cdot 7.54H_2O$ (**2**), and $[Cd(L)_2(H_2O)]\cdot 2H_2O$ (**3**), were obtained and characterized by single-crystal X-ray diffraction, as well as IR spectroscopy. Structure analysis shows only 1,10-phen ligand takes part in coordination in complex **2**. Complex **1** possesses a 3D hydrogen-bonded supramolecular network, which are constructed by the linkage of neutral mononuclear $[Cd(L)_2(H_2O)_4]$ molecules via abundant O–H···O hydrogen-bonds. Compared with **1**, complex **2** features a 2D layer structure, which is made up of 1D tubes consisting of helical chains via π-π interactions. Complex **3** displays a 3D metal-organic framework with $\{6^5\cdot 8\}$ topology. The results reveal that different N-donor auxiliary ligands have a subtle effect on the final structures of coordination supramolecules. Moreover, the solid photoluminescent property of **2** was also studied at room temperature.

1. Introduction

In the past decades, considerable research efforts have been devoted to coordination supramolecules in virtue of their fascinating structures, as well as their intriguing properties and potential applications [1–5]. To effectively achieve aforementioned goals, the judicious choice of the metal ions/clusters and organic ligands is crucial [6,7]. In contrast to limited metal ions/clusters, theoretically numerous organic ligands play more important roles in determining the target coordination supramolecular structures and structure-driven properties due to their diversities of bridging units, the flexibility of the molecular backbone, conformational preference and symmetry of organic ligands [8–11]. For this reason, the prospect of tuning the properties via change of organic ligands provides an impetus for further research on coordination supramolecular architectures [12].

On the other hand, carboxylate ligands with specific conformation, such as tripodal, linear geometries, etc., have been widely used in the construction of coordination supramolecules, especially porous coordination supramolecules, due to their various coordination modes and good coordination capacities [13,14]. Besides carboxylate ligands, N-donor ligands are another class of excellent ligands acting as either organic linkers or terminal ligands [15]. Naturally, a combination of carboxylate and N-donor ligands, i.e. so-called mixed-ligands, provides more possibility to construct the expected coordination supramolecules [16–18]. For our research group, we have been engaged in the construction of coordination supramolecules with L-shaped 1-carboxymethylpyridinium-4-carboxylate (L) ligands and obtained some meaningful results [19–21]. Based on the above analysis and as a continuation of research, we select L-shpaed L ligand as a primary ligand and three different N-donor ligands, namely, 2,2′-bipy, 1,10-phen, and 4,4′-bipy, as auxiliary ligands to construct coordination supramolecules (Scheme 1), simultaneously exploring the influence of N-donor ligands on achieving different dimensional and topological structures. Herein, we report the synthesis and crystal

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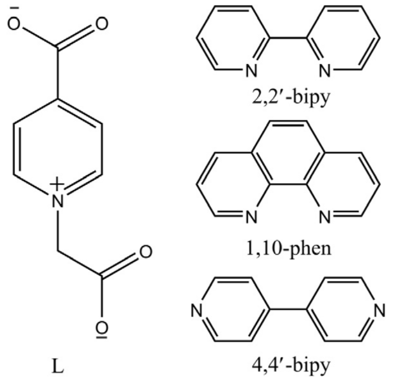

Scheme 1. Structures of L and N-donor ligands used in this work.

structures of three Cd(II) complexes [Cd(L)$_2$(H$_2$O)$_4$] (**1**), [Cd(L)$_2$(1,10-phen)]·7.54H$_2$O (**2**), and [Cd(L)$_2$(H$_2$O)]·2H$_2$O (**3**), as well as the fluorescent property of **2**.

2. Experimental

2.1. Materials and measurements

All materials were reagent grade, obtained from commercial sources and used without further purification. The ligand L was synthesized according to the method reported previously [22]. Solvents were dried by standard procedures. Elemental analyses (C, H, N) were carried out on a Perkin-Elmer 240C elemental analyser. Infrared spectra were recorded in the range of 4000–400 cm^{-1} on a Nicolet 380 FT-IR spectrometer using KBr Pellets. Powder X-ray diffraction (PXRD) were measured at room temperature on a Rigaku Ultima IV diffractometer with graphite monochromatic Cu Kα radiation (λ = 0.15418 nm) at 40 kV and 40 mA. Simulated powder patterns was based on single crystal data and calculated using the Mercury software [23]. The luminescent spectra for the solid samples were recorded at room temperature on a Hitachi F-4600 FL spectrophotometer.

2.2. Synthesis

2.2.1. Synthesis of complex [Cd(L)$_2$(H$_2$O)$_4$] (1)

Cd(NO$_3$)$_2$·4H$_2$O (15.4 mg, 0.05 mmol), L (12.9 mg, 0.05 mmol) and 2,2′-bipy (7.8 mg, 0.05 mmol) were dissolved in a water-ethanol (2:1 v/v) mixture (6 mL) and then stirred for 10 min at room temperature. Colorless lamellar crystals suitable for X-ray diffraction analysis were isolated by slow diffusion of acetone into the clear filtrate for one month. Yield: 32%. Anal. Calcd for C$_{16}$H$_{20}$CdN$_2$O$_{12}$: C, 35.28; H, 3.70; N, 5.14. Found: C, 35.34; H, 3.57; N, 5.09. IR (KBr, cm^{-1}): 3371(m), 3037(m), 1633(vs), 1603(s), 1561(s), 1403(s), 1371(vs), 1290(s), 1190(m), 918(w), 836(m), 781(m), 720(m), 577(w).

2.2.2. Synthesis of complex [Cd(L)$_2$(1,10-phen)]·7.54H$_2$O (2)

Colorless needle-like crystals of compound **2** were prepared as similarly to **1**, except for the use of 1,10-phen (9.9 mg, 0.05 mmol) instead of 2,2′-bipy. Yield: 78%. Anal. Calcd for C$_{28}$H$_{35.08}$CdN$_4$O$_{15.54}$: C, 42.64; H, 4.48; N, 7.10. Found: C, 42.70; H, 4.37; N, 7.09. IR (KBr, cm^{-1}): 3378(m), 3043(m), 1623(vs), 1556(m), 1362(vs), 1194(w), 1140(w), 853(w), 819(w), 786(w), 719(m).

2.2.3. Synthesis of complex [Cd(L)$_2$(H$_2$O)]·2H$_2$O (3)

Colorless needle-like crystals of compound **3** were prepared as similarly to **1**, except for the use of 4,4′-bipy (7.8 mg, 0.05 mmol) instead of 2,2′-bipy. Yield: 14%. Anal. Calcd for C$_{16}$H$_{18}$CdN$_2$O$_{11}$: C, 36.48; H, 3.44; N, 5.32. Found: C, 36.44; H, 3.37; N, 5.39. IR (KBr, cm^{-1}): 0.3369(s), 3121(s), 3051(s), 1620(vs), 1558(vs), 1462(m), 1372(vs), 1213(m), 1192(m), 922(w), 874(w), 826(m), 716(s), 667(s), 584(m), 446(m).

2.3. X-ray crystallography

The X-ray diffraction measurements were performed on the Bruker Smart ApexII CCD diffractometer for complexes **1**–**3** with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Empirical absorption corrections were applied to the data using the multi-scan program SADABS [24]. The structures were all solved by direct method using SHELXS-97 program [25] and refined by the full-matrix least-square method on F^2 with the SHELXL-97 program [26]. Anisotropic thermal parameters were applied to all the non-hydrogen atoms. All hydrogen atoms were inserted at idealized positions and refined using a riding model isotropically except for the H atoms of H$_2$O molecules. The H atoms of water molecules in complexes **1** and **3** were located in a difference map, whereas the H atoms of guest water molecules in **2** have not been added. All calculations were carried out using the SHELXTL crystallographic software package [27]. Details of the crystal parameters, data collection and refinement for complexes **1**–**3** are summarized in Table 1, selected bond lengths and angles with their estimated standard deviations are given in Table 2.

3. Results and discussion

3.1. Description of the crystal structures

3.1.1. Complex [Cd(L)$_2$(H$_2$O)$_4$] (1)

Single-crystal X-ray crystallographic analysis reveals that **1** is a mononuclear complex of formula [Cd(L)$_2$(H$_2$O)$_4$], crystallizing in the monoclinic crystal system with $P2_1$ space group. As shown in Fig. 1a, the Cd(II) ion is coordinated by six O atoms from two L ligands and four coordinated water molecules, leading to a *trans*-octahedron coordination environment. Obviously, the N-donor 2,2′-bipy ligand does not exist in complex **2** and the L ligands act only as simple monodentate terminal ligands using the carboxyl groups to directly connect with the pyridyl group rather than bridging ligands. The Cd–O bond lengths are in the range of 2.2255(18) Å to 2.4064(17) Å, which are longer than the corresponding M–O ones reported in analogues [M(L)$_2$(H$_2$O)$_4$] (M = Co, Mn) [Co–O lengths, 2.040(3)–2.216(3) Å and Mn–O lengths, 2.111(3)–2.319(3) Å] [28], consistent with its expected result. The corresponding selected bond distances and angles are listed in Table 2.

On the other hand, there are abundant proton donors O—H and proton acceptors O from water molecules and carboxyl groups of L ligands, which are the source of the abundant hydrogen bonds in the crystal of **1**. As listed in Table S1 (ESI), there are eight types of hydrogen bonds, among which there is only one intramolecular hydrogen bonding [O2W···O4 distance, 2.715(3) Å] with the graph-set symbol of S(6) [29]. Another seven intermolecular hydrogen bonds can be further divided into three categories according to the hydrogen bonding types. Firstly, two carboxylate oxygen atoms acting as bifurcate proton acceptors from two different mononuclear units and two coordinated water molecules serving as proton donors from another two different mononuclear units generate a cyclic hydrogen bonding motif with graph-set $R_4^2(8)$ [O1W···O1#1 distance, 2.643(3) Å; O1W···O5#2 distance, 2.706(3) Å; O4W···O1#3 distance, 2.683(3) Å; and O4W···O5#4 distance, 2.696(3) Å (symmetry code: #1 −x, y + 1/2, −z + 1; #2 −x − 2, y − 1/2, −z + 1; #3 −x, y + 1/2, −z + 2; #4 −x − 2, y − 1/2, −z + 2]. In another word, the cyclic hydrogen bonding motif linked four mononuclear units together along criss-cross