Two Cadmium(II) Complexes with Polymeric 2D Layer and Discrete Mononuclear Motifs: Syntheses, Crystal Structures, and Fluorescent Properties

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Abstract—Two new 1,3-bi(4-pyridyl)propane-based cadmium(II) complexes, [Cd(Bpp)\textsubscript{2}(Nas)\textsubscript{2}]\textsubscript{n} (I) and [Cd(Bpp)\textsubscript{2}(Na)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}] (II) (Bpp = 1,3-bi(4-pyridyl)propane, Nas\textsuperscript{−} = 2-aminonaphthalene-1-sulfonate, and Na\textsuperscript{−} = 1-naphthoate) (CIF files CCDC nos. 1429589 (I), 1429590 (II)) have been hydrothermally synthesized by varying carboxylate- or sulfonate-containing coligands. Structural analyses reveal that, complex I with monodentate Nas\textsuperscript{−} ligands exhibits a two-dimensional (2D) layered motif extended by equatorial Bpp connectors. By contrast, complex II modified by monodentate Na\textsuperscript{−} ligands exhibit discrete mononuclear structure. Although the Nas\textsuperscript{−}/Na\textsuperscript{−} coligands showed the same monodentate binding modes, the Bpp ligand exhibits bridging or terminal binding modes in I and II, respectively. So it is obvious that the competitive coordination in the present mixed-ligands system is responsible for the aggregation or dissociation of mononuclear structural units. Furthermore, both of the two compounds are linked to 3D supramolecular architecture by intermolecular C–H···O hydrogen bonding or C–H···π stacking interactions, exhibiting strong fluorescent emissions resulting from the ligand-to-metal or Na\textsuperscript{−}-based intraligand charge transfer at room temperature, which can be hopefully used as fluorescent materials.

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INTRODUCTION

Because of their aesthetically fascinating structures of topology [1] and the potential applications such as fluorescent materials [2], magnetic materials [3], selective catalyst [4], gas adsorbents [5], and molecular separation [6], metal organic complexes have been one hot subject of research for many chemists and material scientists. In this aspect, the choice of appropriate ligand is the key to construct complexes with special structure and property. Compared with the rigid ligand, flexible ligand shows better tenability to construct intriguing framework. The incorporating of aliphatic chain between the rigid pyridyl rings increase the flexibility of organic ligand, a series of complexes based on bi(4-pyridyl)alkanes have been reported, including diverse structures from discrete oligomers to high dimensional metal organic frameworks [2, 7–13]. Among of these compounds, bi(4-pyridyl)alkane has displayed two significant features, the organic linkers with variable length exhibit versatile conformations due to free rotation of the C–C σ single bond in the aliphatic chain. On the other hand, bi(4-pyridyl)alkane ligand can act as an organic linker to aggregate metal centers together by bidentate bridging mode with different metallomacrocycles formed by metal ions and bridging ligands, which are increased with increment of the length of aliphatic chain. Obviously, the length of the aliphatic chain plays an key role for the structural motifs of the coordination complexes based on bi(4-pyridyl)alkanes.

Herein, to further investigate the competitive coordination ability of bi(4-pyridyl)alkanes in mixed ligands system, two O-donor-based coligands respectively with functional sulfonate and carboxylate groups, 2-aminonaphthalene-1-sulfonate (HNas) and 1-naphthoic acid (HNa), were chosen as fundamentally building blocks to self-assembly with 1,3-bi(4-pyridyl)propane (Bpp) and inorganic cadmium(II) salts. Obviously, the particular reason for introducing the two different coligands is that the coordination ability of organic sulfonate ligand to metal ion is generally considered weaker than that of the deprotonated carboxylate group. In the present contribution, two novel complexes, [Cd(Bpp)\textsubscript{2}(Nas)\textsubscript{2}]\textsubscript{n} (I) and [Cd(Bpp)\textsubscript{2}(Na)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}] (II) were hydrothermally obtained and structurally

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characterized. Despite the Nas−/Na− coligands showed the same monodentate binding modes, I owns 2D layer motif and II exhibits discrete mononuclear structure, both of which are linked to 3D supramolecular architecture by intermolecular C–H⋯O hydrogen bonding or C−H⋯π stacking interactions. Furthermore, both compounds exhibit strong fluorescent emissions at room temperature, which primarily resulted from ligand-to-metal or the intraligand electronic transfer ascribed of Na− anion.

EXPERIMENTAL

Reagents and instruments. HNas and HNa were purchased from Acror and other analytical-grade starting materials were obtained commercially and used as received without further purification. Doubly deionized water was employed for the conventional synthesis. IR spectra were collected in a range of 4000−400 cm−1 region on a Nicolet IR−200 spectrometer with KBr pellets. Elemental analyses for C, H and N were determined on a Perkin-Elmer 2400C elemental analyzer. Thermogravimetric analysis (TGA) experiments were carried out on a Shimadzu simultaneous DTG-60A thermal analysis instrument with a heating rate of 10°C min−1 from room temperature to 800°C under a nitrogen atmosphere (flow rate 10 mL min−1). Fluorescence spectra of the polycrystalline powder samples of I and II were performed on a Fluorolog-3 fluorescence spectrophotometer from Horiba Jobin Yvon at room temperature.

Synthesis of I. A mixture of HNas (89.3 mg, 0.4 mmol), Bpp (39.6 mg, 0.2 mmol), CdAc2 · 2H2O (106.6 mg, 0.4 mmol), NaOH (24.0 mg, 0.6 mmol), and doubly deionized water (12 mL) were sealed in a 23 mL stainless steel vessel. Then the mixture was heated at 140°C for 72 h under autogenous pressure. After the mixture was cooled to room temperature, colorless block-shaped crystals suitable for single-crystal X-ray diffraction analysis were isolated directly, washed with ethanol, and dried in air. The yield was 46% based on Cd salts.

For C48H46N4O6Cd
anal. calcd., %: C, 57.95; H, 4.65; N, 8.81.
Found, %: C, 57.92; H, 4.67; N, 8.83.

IR (ν, cm−1): 3445 ν(N−H), 3340 ν(N−H), 3046 ν(C−H), 1220 ν(SO2), 1160 ν(SO2), 619 ν(SO3).

Synthesis of II. Pink block-shaped crystals of II suitable for single-crystal X-ray diffraction analysis were obtained by adopting the similar procedures to those of I only with HNa instead of HNas. The yield was 33% based on Cd salts.

For C48H46N4O6Cd
anal. calcd., %: C, 64.97; H, 5.23; N, 6.31.
Found, %: C, 65.15; H, 5.12; N, 6.50.

IR (ν, cm−1): 3430 ν(O−H), 3060 ν(C−H), 1607 νas(COO−), 1559 νs(COO−), 1415 ν(COO−), 1370 ν(COO−).

X-ray diffraction analysis. Single-crystal X-ray diffraction data for I and II were collected on a computer-controlled Bruker APEX-II CCD diffractometer equipped with graphite-monochromated MoKα radiation with radiation wavelength 0.71073 Å by using ω−φ scan mode at room temperature. Semiempirical multiscan absorption corrections were applied using SADABS [14] and the program SAINt [15] was used for integration of the diffraction profiles. Both structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs [16]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically. Details for crystallographic data were listed in Table 1, and selected bond lengths and angles were given in Table 2. Hydrogen-bonding parameters for I and II were shown in Table 3. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 1429589 (I) and 1429590 (II); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Phase-pure crystals of I and II were successfully prepared under similar hydrothermal conditions in basic medium. Obviously, the introduction of aqueous NaOH solution is to make HNas/HNa coligands deprotonation and facilitate their coordination with Cd2+ ion. Additionally, complexes I and II are air stable, insoluble in common organic solvents and can retain their crystalline integrity at ambient conditions for a considerable length of time.

In the IR spectra, the weak absorption peaks located at 3445 and 3340 cm−1 for I could be ascribed to the stretch vibrations of exocyclic amino group of Nas− anion. By contrast, the O−H stretching vibrations of water molecule lead to an adsorption band centered at 3430 cm−1 in II. In addition, the weak absorption peaks appeared at 3046 for I and 3060 cm−1 in II should be assigned to the C−H stretching vibrations of aromatic ring. An absence of a characteristic band at 1675 cm−1 in II indicates the complete deprotonation of HNa ligand by NaOH [17], which is consistent with the results of single crystal structure determinations. Furthermore, the adsorption bands at 1220, 1160 and