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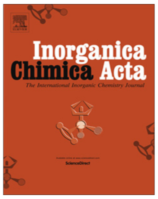

Synthesis, structures and photoluminescence of three d^{10} 5-aminonicotinate and 5-aminoisophthalate coordination polymers with bilayer structures

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ABSTRACT

Base on ligands 5-aminonicotinic acid and 5-aminoisophthalic acid, three novel d^{10} coordination polymers $[Zn(ant)_2]_n$ (**Zn-ant**) (ant = 5-aminonicotinate anion), $[CdBa(aip)_2(H_2O)_2]_n$ (**CdBa-aip**) and $[Cd_3(aip)_2(C_2O_4)(H_2O)_6]_n$ (**Cd-aipox**) (aip = 5-aminoisophthalate anion) are obtained by hydrothermal reactions, and characterized by means of FT-IR spectra, elemental analysis, single-crystal X-ray diffraction analysis and X-ray powder diffraction techniques. Thermogravimetric analysis is also carried out in order to investigate the stability of compounds Compound **Zn-ant** exhibits a 2D interlaced-bilayer structure. While compounds **CdBa-aip** and **Cd-aipox** feature the unusual 2D pillared-bilayer structures formed by the cross-linking of the aip and oxalate units. Considering the complicated hydrogen bonds and interlayer $\pi\cdots\pi$ stacking interactions, all of the three compounds are finally packed into three-dimensional supramolecular networks. The deprotonating reagent-induced effect is responsible for the generation of two different compounds **CdBa-aip** and **Cd-aipox**. In addition, the photoluminescent properties of three compounds have also been investigated in the solid state at room temperature.

1. Introduction

Luminescent coordination polymers (CPs) containing d^{10} metal ions with closed-shell electronic configurations have drawn enormous interest due to their intriguing coordination architectures and their potential applications in various fields including catalysis, photochemistry, fluorescence, biological properties, etc [1]. From the viewpoint of the synthetic strategy of crystal engineering, the suitable selection of organic ligands plays a dominating role on the construction of CPs. Used as a heterocyclic acid with the conjugated structure, 5-aminonicotinic acid (H_2ant) possesses one carboxyl group and one N atom available for coordination to a metal center, and its amino group may contribute to rich hydrogen bonds and the architecture of supramolecular structure. Furthermore, the presence of an amino group between the nitrogen atom and the carboxylate group presumably favors the post-synthetic modification for CPs [2]. To our knowledge, the ligand H_2ant has not been employed to construct any CPs so far. On the other hand, we know that the assembly of the CPs can be modulated by changing the nature or the position of the substituent on an aromatic ring [3]. In comparison, 5-aminoisophthalic acid (H_2aip) can be regarded as an analogue of 5-aminonicotinic acid with respect to the relative disposition of amino groups, in which the pyridine ring of the latter is replaced by the phenyl one, and one carboxyl group is synchronously introduced to the phenyl ring (seeing Scheme 1). Up to now, many *d*-block transition metal CPs constructed from 5-aminoisophthalatic acid have been reported previously [4]. From the other hand, based on 5-aminoisophthalatic acid, an attempt to construct lanthanide [5], 3*d*-4*f* heterometallic [6] and 3*d*-3*d* heterometallic CPs [7] with new structural features has also been performed.

With regard to the dynamic coordination assemblies from the organic ligands, the choice of the solvent, counter ion, template, pressure, temperature, and pH value etc, is also proved to be a facile approach to induce structural diversity, polymorphism, dynamic transformation, and physicochemical properties of the related CPs. However, considering the reactive nature of the carboxylic acid, the influence of the different deprotonating reagents on the assemblies of CPs based on 5-aminoisophthalic acid is far less explored.

Inspired by all the aforementioned considerations, the hydrothermal reaction of zinc nitrate hexahydrate and H_2ant in the presence of NaOH resulted in the formation of a new zinc

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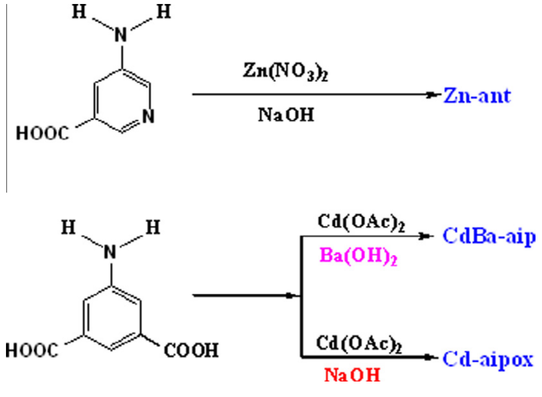

Scheme 1. General synthesis path for compounds **Zn-ant**, **CdBa-aip** and **Cd-aipox**.

coordination polymer $[Zn(ant)_2]_n$ (**Zn-ant**) (ant = 5-aminonicotinate anion), which presents the first example of d^{10} CPs constructed from 5-aminonicotinic acid. At the same time, under the similarly hydrothermal reaction conditions, the same amounts of cadmium acetate dihydrate and H_2aip in the presence of the deprotonating reagents $Ba(OH)_2$ and NaOH generate two compounds $[CdBa(aip)_2(H_2O)_2]_n$ (**CdBa-aip**) and $[Cd_3(aip)_2(C_2O_4)(H_2O)_6]_n$ (**Cd-aipox**) (aip = 5-aminoisophthalate anion), respectively. The obtained results demonstrate a useful guideline toward constructing the different d^{10} CPs based on carboxylic acids under the various deprotonating reagents. Herein, we present the synthesis, characterization and photoluminescence properties of these new d^{10} CPs with the ligands H_2ant and H_2aip.

2. Experimental

2.1. Materials and methods

All reagents are commercially available and used without further purification. Elemental analyses (C and H) are performed on a Perkin-Elmer 2400 Series II CHNS/O elemental analyzer. FT-IR spectra are recorded in the range 400-4000 cm^{-1} on a Perkin-Elmer FT-IR spectrometer using KBr pellets. TG analysis is performed on a Perkin-Elmer Diamond TG/DTA instrument in flowing air with a heating rate of 10 °C min^{-1}. X-ray powder diffraction (XRPD) patterns are recorded on an X-ray diffractometer (Rigaku D/Max 2200PC). Emission and excitation spectra are obtained on an Edinburgh Instruments analyzer model FLS920 spectrofluorometer.

2.2. Synthesis of compounds

2.2.1. $[Zn(ant)_2]_n$ (**Zn-ant**)

A mixture of zinc nitrate hexahydrate (2.0 mmol), NaOH (3.0 mmol), and 5-aminonicotinic acid (3.0 mmol) in 20 mL H_2O are stirred for 15 min at room temperature. The mixture is then transferred into a 40 mL Teflon-lined stainless-steel vessel, and heated at 210 °C for four days under autogenous pressure. After the reaction mixture have slowly cooled down to room temperature, brown sheet crystals of **Zn-ant** are filtered off, washed with distilled water, and dried in air. Yield: ~80%. Elemental analysis for $C_{12}H_{10}N_4O_4Zn$: *Anal.* Calc. C, 42.44; H, 2.97; N, 16.50. Found: C, 42.38; H, 2.88; N, 16.45%. IR (KBr pellet, cm^{-1}): 3381m, 3337m, 3232m, 3089w, 2926w, 2858w, 2751w, 2565w, 1849w, 1660m, 1621s, 1575s, 1475m, 1452m, 1419s, 1393s, 1349w, 1328w, 1307m, 1289s, 1174s, 1133m, 1120w, 1027s, 965w, 907s, 864m, 835m, 822s, 791s, 716m, 692m, 632w, 572w, 549w, 528w, 464w, 448w, 430w.

2.2.2. $[CdBa(aip)_2(H_2O)_2]_n$ (**CdBa-aip**)

A mixture of cadmium acetate dihydrate (3.0 mmol), $Ba(OH)_2$ (3.0 mmol), and 5-aminoisophthalic acid (3.0 mmol) in 20 mL H_2O are stirred for 15 min at room temperature. The mixture is then transferred into a 40 mL Teflon-lined stainless-steel vessel, and heated at 210 °C for four days under autogenous pressure. After the reaction mixture have slowly cooled down to room temperature, white block crystals of **CdBa-aip** are filtered off, washed with distilled water, and dried in air. Yield: ~45%. Elemental analysis for $C_{16}H_{14}N_2O_{10}CdBa$: *Anal.* Calc. C, 29.84; H, 2.19; N, 4.35. Found: C, 29.78; H, 2.09; N, 4.27%. IR (KBr pellet, cm^{-1}): 3437m, 3413m, 3312w, 3269w, 2920w, 2851w, 1680m, 1617m, 1569s, 1545s, 1476m, 1453w, 1395s, 1365s, 1329s, 1263m, 1113w, 1027m, 999m, 966m, 938w, 892m, 809w, 795m, 778m, 767w, 731m, 678w, 620w, 559w, 506w.

2.2.3. $[Cd_3(aip)_2(C_2O_4)(H_2O)_6]_n$ (**Cd-aipox**)

A mixture of cadmium acetate dihydrate (3.0 mmol), NaOH (6.0 mmol), and 5-aminoisophthalic acid (3.0 mmol) in 20 mL H_2O are stirred for 15 min at room temperature. The mixture is then transferred into a 40 mL Teflon-lined stainless-steel vessel, and heated at 210 °C for four days under autogenous pressure. After the reaction mixture have slowly cooled down to room temperature, rufous prism crystals of **Cd-aipox** are filtered off, washed with distilled water, and dried in air. Yield: ~60%. Elemental analysis for $C_{18}H_{22}N_2O_{18}Cd_3$: *Anal.* Calc. C, 24.25; H, 2.49; N, 3.14. Found: C, 24.16; H, 2.41; N, 3.06%. IR (KBr pellet, cm^{-1}): 3425m, 3269m, 3183w, 2922w, 1640m, 1610w, 1556s, 1475m, 1449w, 1379s, 1321s, 1260m, 1138w, 1100w, 1037m, 999w, 976m, 932w, 889w, 805m, 779m, 735m, 669w, 588w, 451w.

2.3. X-ray crystallography

Crystal data are collected on an Xcalibur, Eos, Gemini diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å). Data reduction is accomplished by the CRYSALISPRO (Oxford Diffraction Ltd., Version 1.171.33.55) program. The structures are solved by direct method and refined by a full matrix least-squares technique based on $|F|^2$ using SHELXL 97 program. All of the non-hydrogen atoms are refined anisotropically. The organic hydrogen atoms are generated geometrically, the aqua hydrogen atoms are located from difference maps and refined with isotropic temperature factors. The crystallographic data and experimental details for the structural analyses are summarized in Table 1.

3. Results and discussion

3.1. Structural description of $[Zn(ant)_2]_n$ (**Zn-ant**)

Single crystal X-ray diffraction study shows that **Zn-ant** crystallizes in the orthorhombic space group $P2_12_12_1$. As depicted in Fig. 1 (seeing the parts represented in “ball-and-stick” model), the asymmetric unit contains one crystallographically independent Zn(II) ion and two ant ligands, Zn1 is pentacoordinated by two pyridyl N atoms (N3, N1A) from two different ant ligands, and three oxygen atoms (O1, O2, O3C) from two carboxylate groups of the other two different ant ligands. As a result, Zn1 ion exhibits a distorted squarepyramidal environment with the Zn–O and Zn–N bond lengths falling in the range of 1.9608(23)–2.4365(24) Å and 2.0317(27)–2.0628(26) Å, respectively, which are in good agreement with the bond lengths observed in other Zn(II) derivatives [8].

It is noticeable that the carboxylate groups of two different ant ligands adopt the chelate and monodentate coordination modes, and each ant ion acting as a bridge-linking ligand coordinates to