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Research paper

Synthesis, structural characterization and photoluminescence property of two Zn^{2+}/In^{3+}-4,4′-oxydiphthalhydrazidate complexes

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ABSTRACT

Under the hydrothermal conditions, two new 4,4′-oxydiphthalhydrazidate-containing compounds $[Zn_2(odpth)_2(phen)_2]\cdot H_2O$ **1** and [In(odpth)(ox)(phen)] **2** (odpth = 4,4′-oxydiphthalhydrazidate, phen = 1,10-phenanthroline, ox = oxalate), were obtained. Note that odpth ligand was derived from the hydrothermal *in situ* acylation reaction between 4,4′-oxydiphthalic acid (odpha) with $N_2H_4\cdot H_2O$. In compound **1**, the odpth ligands exhibit a μ_2-bridging mode, which link Zn(II) centers into a 1-D chained structure with ancillary phen molecules. Interestingly, in compound **2**, the ox ligands exhibit a μ_2-bridging mode, which link In(III) centers into a different 1-D chained structure with ancillary odpth and phen molecules. Although they are only 1-D chained coordination polymers, they all further self-assemble into the interesting supramolecular networks *via* π···π stacking or hydrogen-bonded interactions. The photoluminescence analyses indicate that the compounds in the different states (in the solid state or in aqueous solution) may exhibit different emission behaviors.

1. Introduction

Due to the structural diversity, and potential applications in porosity, catalysis and optics, considerable attention has been paid to the design and synthesis of novel coordination polymers [1–4]. In the formation of the framework structures for coordination polymers, the organic ligands play a key role. So far, most of the used organic ligands are commercially available or presynthesized. Recently, the hydro (solvo)thermal ligand *in situ* preparations offer a new approach to obtain the novel organic ligands [5–9]. So-called *in situ* ligand synthesis is when ligand precursors are used in place of the ligands to react with metal ions, finally producing the ligand-containing complexes. Compared with the conventional synthetic method, *in situ* ligand synthesis possesses the following merits: simplicity, effectiveness and environmental friendliness. To date, several ligand *in situ* reactions have been observed, and applied to construct a few novel coordination polymers [10–17]. In 2004, Xu reported first the diacylhydrazidate-bridged coordination polymers obtained by applying the *in situ* acylation reaction between pyromellitic acid and hydrazine hydrate [18,19]. Based on the following considerations, the current investigation for our group is focused on the structural characterization of a series of metal-acylhydrazidate complexes. (i) The diversity of the acylhydrazide molecule. Organic polycarboxylic acids containing at least a pair of neighboring carboxyl groups can *in situ* acylate with hydrazine hydrate (see Scheme 1), so the acylhydrazide molecule is a big family. (ii) The diversity of the coordination mode for the acylhydrazide molecule. The N and O atoms in acylhydrazide molecule can all act as the donors to coordinate to the metal centers. Moreover, these atoms can also act as the hydrogen-bonded donors/acceptors, extending the low-dimensional molecules into high-dimensional supramolecular networks. (iii) The potential presence of multiple kinds of charge transfer paths in acylhydrazidate-containing complexes. So far, some novel di(mono) acylhydrazidate-bridged coordination polymers with 1-D, 2-D and 3-D structures have been further prepared by using various aromatic polycarboxylic acids to replace pyromellitic acid [20–35].

Interestingly, some of them exhibit excellent photoluminescence properties in the solid state, and emit the different light upon excitation: red light for [Cu(pth)] (pth = phthalhydrazidate) (λ_{em} = 636 nm) [20]; yellow for [Pb(mpdh)] (mpdh = 6-methylpyrinde-2,3-dicarboxylhydrazidate) (λ_{em} = 600 nm) [26]; green for $[Zn(pdh)_2(H_2O)_2]$

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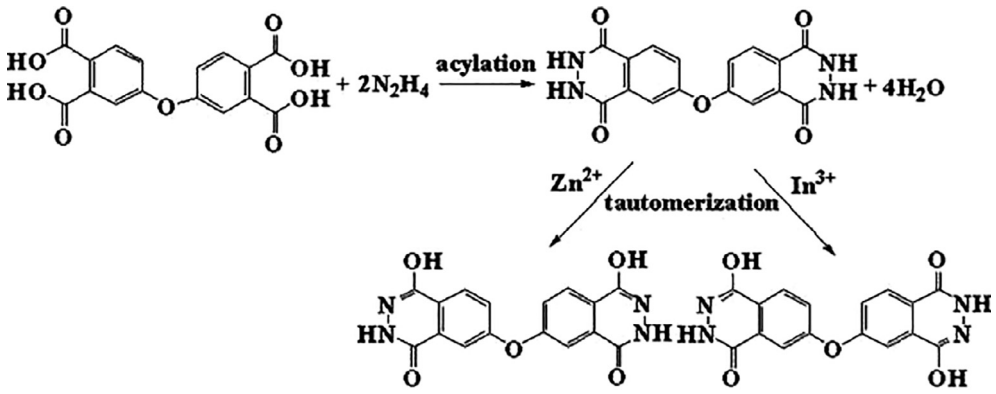

Scheme 1. The detailed formation process of the odpth molecules in the title compounds.

(pdh = pyrinde-2,3-dicarboxylhydrazidate) (λ_{em} = 520 nm) [27]; blue for [H(dcpth)] (dcpth = 4,5-dichlorophthal-hydrazidate) (λ_{em} = 460 nm) [23]. The different emission behaviors for metal-acylhydrazidate compounds are due to the difference in their charge transfer paths. For example, the red-light emission of [Cu(pth)] is assigned to the charge transfer of the donors (N, O) of the pth ligands to copper(I) centers [20]; the green-light emission of $[Zn(pdh)_2(H_2O)_2]$ (pdh = pyrinde-2,3-dicarboxylhydrazidate) is ascribed to the charge transfer from the π* orbital of a pyridine ring moiety to the π orbital of an acylhydrazidate ring moiety [27]. Recently, we found that metal-acylhydrazidate complexes in aqueous solutions also emit light [27–30,33,34]. More interestingly, in aqueous solutions they have different emissions from those observed in the solid state. In order to reveal why this situation occurred, we will report the structural characterization of two new 4,4′-oxydiphthalhydrazidate-containing compounds $[Zn_2(odpth)_2(phen)_2]\cdot H_2O$ **1** and [In(odpth)(ox)(phen)] **2** (odpth = 4,4′-oxydiphthalhydrazidate, phen = 1,10-phenanthroline, ox = oxalate) in this article. Note that odpth derived from the hydrothermal acylation reactions between odpha and $N_2H_4\cdot H_2O$ (Scheme 1).

2. Experimental

2.1. Materials and physical measurement

All chemicals are of regent grade quality, obtained from commercial sources and used without further purification. Elemental analysis was performed on a Perkin-Elmer 2400LS II elemental analyzer. Infrared (IR) spectrum was recorded on a Perkin Elmer Spectrum one FTIR spectrometer in 4000–400 cm^{-1} region with a resolution of 4 cm^{-1} by accumulating 32 scans, using a powdered sample on a KBr plate. Powder X-ray diffraction (XRD) data were collected on a Rigaku/max-2550 diffractometer with Cu-K_α radiation (λ = 1.5418 Å). Thermogravimetric (TG) behavior was investigated on a Perkin-Elmer TGA-7 instrument with a heating rate of 10 °C min^{-1} in air. Fluorescence spectrum was obtained on a LS 55 fluorescence/phosphorescence spectrophotometer at room temperature.

2.2. Synthesis of the title compounds

$[Zn_2(odpth)_2(phen)_2]\cdot H_2O$ 1: A mixture of $Zn(CH_3COO)_2\cdot 2H_2O$ (110 mg, 0.5 mmol), odpha (155 mg, 0.5 mmol), $N_2H_4\cdot H_2O$ (0.16 mL), phen·H_2O (99.0 mg, 0.5 mmol), H_2ox (63.0 mg, 0.5 mmol) and H_2O (15 mL) was stirred for 2 h at room temperature. Its pH was then adjusted to 8 with an aqueous solution of $N_2H_4\cdot H_2O$ (80%). The resulting mixture was sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 170 °C for 4 days, after which it was cooled over 12 h to room temperature, yellow block-shaped crystals were obtained by filtration, washed by distilled water and air-dried to give a 30% yield (based on Zn(II)). Anal. Calcd $C_{56}H_{34}N_{12}O_{11}Zn_2$ **1**: C 56.92, H 2.90, N 14.22. Found: C 56.07, H 3.04, N 14.04%. IR (cm^{-1}): 1655s, 1593s, 1490s, 1387w, 1341w, 1259s, 1217m, 1145w, 1063m, 950m, 826m, 734m, 651m, 523m.

[In(odpth)(ox)(phen)] 2: The yellow block crystals of **2** were obtained by a similar hydrothermal self-assembly to that of **1** except that $InCl_3\cdot 4H_2O$ (147 mg, 0.5 mmol) replaced $Zn(CH_3COO)_2\cdot 2H_2O$ (pH = 5 adjusted by saturated H_2ox solution). Yield: *ca.* 40% based on In(III). Anal. Calcd $C_{30}H_{17}N_6O_9In$ **2**: C 49.41, H 2.49, N 11.52. Found: C 49.45, H 2.52, N 11.54%. IR (cm^{-1}): 1664 s, 1430 m, 1344 m, 1258 s, 1063 m, 943 m, 805 s, 731 s, 650 w, 496 m, 433 w.

2.3. X-ray crystallography

Data were collected with Mo-K_α radiation (λ = 0.71073 Å) on a Siemens SMART CCD diffractometer for compounds **1** and **2**. With SHELXTL program, the structures of **1–2** were solved using direct methods. The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement; the hydrogen atoms of the organic ligands were localized in their calculated positions and refined using the riding model in compounds **1** and **2**, while the hydrogen atoms of the water molecule for compound **1** were localized in their calculated positions by the program OLEX2 [36,37]. The structure was then refined on F^2 using SHELXL-2014. CCDC numbers are 1569652, 1,569,466 for compounds **1** and **2**, respectively. The crystallographic data for **1–2** are summarized in Table 1. The C—O and C—N distances in acylhydrazide ring are listed in Table 2. The hydrogen-bonded parameters are listed in Table 3.

Table 1
Crystallographic data for the title compounds.

Compound	1	2
Formula	$C_{56}H_{34}N_{12}O_{11}Zn_2$	$C_{30}H_{17}N_6O_9In$
M/g mol^{-1}	1181.69	720.32
Crystalsystem	Monoclinic	Triclinic
Space group	$P2_1$	P-1
a/Å	9.0001(10)	8.7820(3)
b/Å	12.6448(14)	10.6015(4)
c/Å	20.724(2)	14.9880(5)
α/ °		76.2000(10)
β/°	90.946(4)	82.0920(10)
γ/°		83.3480(10)
V/Å^3	2358.2(4)	1337.24(8)
Z	2	2
D_c/g cm^{-3}	1.664	1.789
/mm^{-1}	1.101	0.957
Reflections collected	23,571	34,854
Unique reflections	8546	4888
R_{int}	0.0319	0.0305
Gof	1.065	1.084
R_1, $I > 2\sigma(I)$	0.0579	0.0206
wR_2, all data	0.1279	0.0566