

Non-covalently aggregated zinc and cadmium complexes derived from substituted aromatic carboxylic acids: Synthesis, spectroscopy, and structural studies [☆]



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ABSTRACT

Mononuclear zinc carboxylates $[Zn(L)(2,2'\text{-bpy})_2](ClO_4)(nH_2O)$ (**1–4**) (LH = 3-aminobenzoic acid (3-abaH) (**1**), salicylic acid (saH₂) (**2**), 3,5-diisopropylsalicylic acid (dipsaH₂) (**3**), and 3-methyl-2-thiophenecarboxylic acid (3-Me-2-TCAH) (**4**)) and cadmium carboxylates $[Cd(tipba)(2,2'\text{-bpy})_2](tipbaH)$ (**5**) (tipaH = 2,4,6-triisopropylbenzoic acid), $[Cd(2,2'\text{-bpy})_2(2\text{-TCA})(ClO_4)]$ (**6**) (2-TCAH = thiophene-2-carboxylic acid) and $\{[Cd(2,2'\text{-bpy})_2(3\text{-Me-2-TCA})]\{Cd(2,2'\text{-bpy})_2(3\text{-Me-2-TCA})(H_2O)\}\}(ClO_4)_2$ (**7**) have been synthesized from the reaction of the metal precursor complex $[M(OAc)(2,2'\text{-bpy})_2](ClO_4)(H_2O)$ (M = Zn and Cd) with the respective aromatic carboxylic acid in methanol at ambient conditions. Complexes **1–7** have been characterized with the aid of elemental analysis and FT-IR, UV-Vis, fluorescence, ¹H NMR spectroscopic methods and further analyzed by single-crystal X-ray diffraction studies. The carboxylate groups show chelating and monodentate coordination behavior in these complexes. While the cadmium ion in **6** is heptacoordinated, the structure of **5** reveals a coordination number of eight with square antiprismatic geometry. Hydrogen bonding patterns in **1–4** and **7** result in a 1-D polymeric structure while **5** is a 2-D layer structure and **6** is a 3-D polymeric structure.

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1. Introduction

Inorganic–organic hybrid compounds with extended structures are of current interest owing to their intriguing structural motifs and interesting electro-conductive, optical and magnetic properties [1–6]. Among these, metal carboxylates have been extensively studied because the carboxylate group can bind to metal ions in various modes, such as monodentate, bidentate and bridging [7–16]. Particularly, zinc carboxylate with nitrogen donor ligands are of interest in biological point of view where zinc-containing active sites of enzymes [17–19]. Among these active sites, the carboxylate groups have been found to exhibit the unidentate, bidentate chelate and bridging modes [20–22]. Zinc acetylsalicylate $[Zn(acsal)_2(H_2O)_2]$ is used as an anti-inflammatory agent [23]. The zinc complex of 3-aminobenzoic acid (3-abaH) is an important substance which shows biological activity and was found to inhibit the carcinogenic effect of N-2-fluorenyl acetamide which is believed to be responsi-

ble for liver tumor in animals [24]. The coordination chemistry of zinc(II) carboxylates has been widely studied and the unusual variability and coordination flexibility of zinc(II) is well established [25–29]. The coordination chemistry of cadmium is important in both biological and non-biological areas. The cadmium ion adapts a wide variety of stereochemical environments with a d¹⁰ electronic configuration [30–31]. Among numerous examples, cadmium(II) complexes with coordination numbers four, five and six are well known, but seven and eight coordinated cadmium(II) has been obtained in a few cases [32–36].

From the coordination chemistry point of view, salicylic acid (saH₂), 3-aminobenzoic acid (3-abaH) and thiophene carboxylic acid (TCAH) are versatile ligands. Salicylate and aminobenzoate anions offer hard and strongly basic donor centers in a ligand geometry that facilitates chelation. The use of a sterically demanding aromatic carboxylic acid, 2,4,6-triisopropyl benzoic acid in these reactions allows the evaluation of steric effects in metal carboxylic acid chemistry. Hydroxyl and amino groups can entertain intra- and/or intermolecular hydrogen bonding to assist formation of aggregated assemblies [37–40]. An interesting characteristic of the TCAH is the presence of three possible coordination sites (two carboxylic oxygen atoms and one heterocyclic sulfur) [41–45].

The introduction of ancillary ligand like 2,2'-bipyridine (2,2'-bpy) has been widely used to impede the aggregation of metal

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centers, owing to the excellent chelating mode of this ligand as well as its ability to provide potential supramolecular contact (π - π stacking interactions) [46]. Owing to these reasons, we have investigated the formation of zinc and cadmium complexes of aminobenzoic, salicylic, and thiophene carboxylic acids in the presence of 2,2'-bipyridine auxiliary ligands. The results obtained are reported in this contribution.

2. Result and discussion

2.1. Synthesis

Metal precursors with a non-coordinating anion, $[M(OAc)(2,2'-bpy)_2](ClO_4)(H_2O)$ ($M = Zn, Cd$) [25,47], were used as starting material along with corresponding carboxylic acids to synthesize all the new zinc and cadmium complexes **1–7** (Scheme 1). The synthesis of new carboxylates have been achieved using a similar synthetic procedure by reacting one equivalent of metal precursor and one equivalent of the corresponding carboxylic acid in a methanol solution (Scheme 1). The products have been obtained in moderate to good yields (~50%) in analytically pure form in each case and characterized by means of FT-IR, UV-Vis absorption, emission and 1H NMR spectroscopic studies. All the compounds were found to be air-stable and also soluble in common organic solvents.

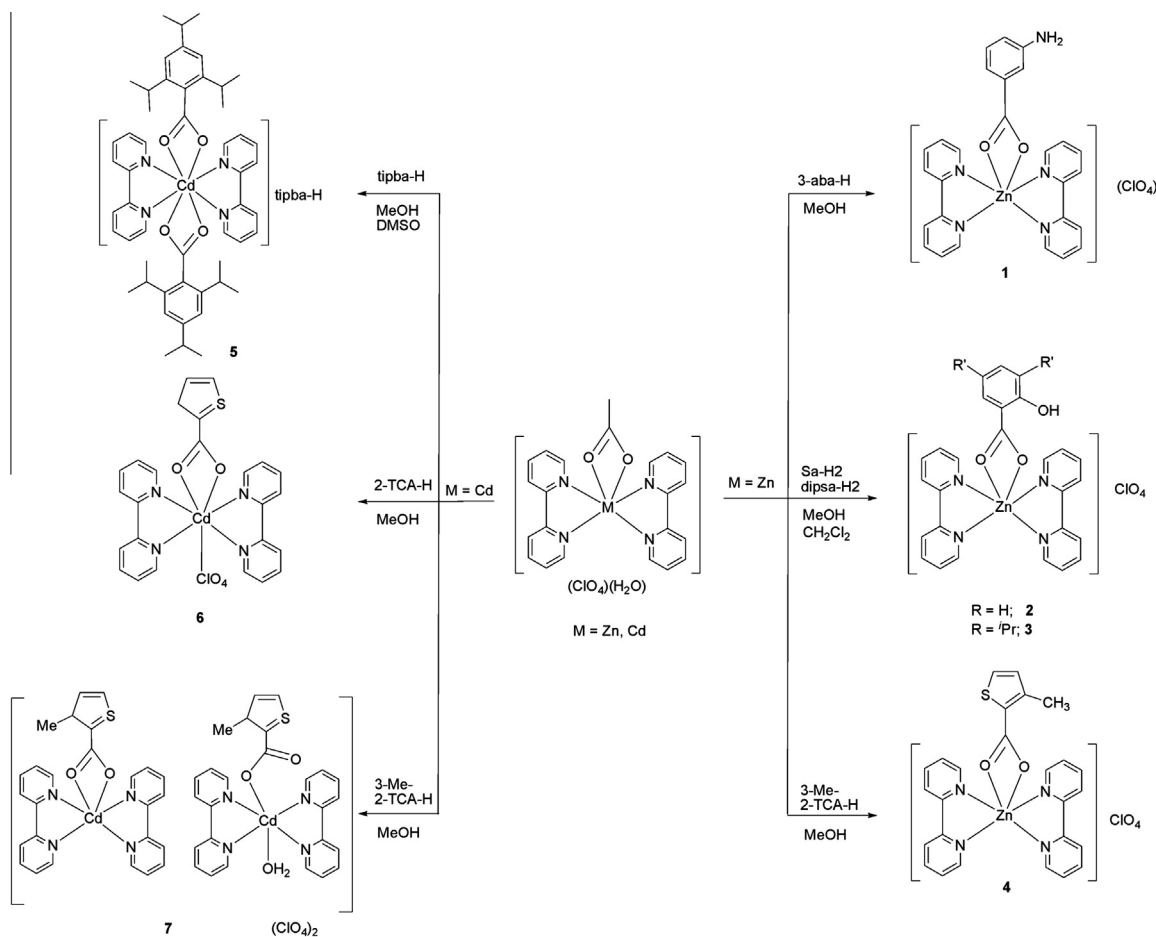
2.2. Spectral characterization

The FT-IR spectrum for compound **1** shows characteristic N-H stretching vibration at around 3370 cm^{-1} . Compounds **2, 3** and **5**

show absorption at around 3400 cm^{-1} corresponding to the presence of hydroxyl group. The infrared spectral peaks at around 3080 cm^{-1} are due to the aromatic C-H vibrations. Additionally, the strong aliphatic C-H vibrations occur at around 2960 cm^{-1} for the isopropyl groups in **3** and **5** and methyl group in **4** and **7**. The $\nu_{as}(COO^-)$ band is observed at around 1605 cm^{-1} , while the $\nu_s(COO^-)$ vibration is observed at 1315 cm^{-1} for **1**. The compounds **2–7** show similar types of vibration frequencies. Strong IR band observed at 1092 cm^{-1} indicates the presence of ClO_4^- anion in all compounds excepting **5**. The UV absorption spectra of all the new complexes are similar; the observed single absorption between 300 and 320 nm could be ascribed to the π - π^* transitions of the 2,2'-bipyridine ligand and/or the aryl rings of the carboxylate ligands.

The emission properties of complexes **1–7** have been studied in dimethyl sulfoxide solution. A single emission was observed in the range of 380–480 nm for **5** in methanol solution at the excitation of 311 nm. It is unlikely that this is an intraligand fluorescent emission but could be attributed to the charge transfer between the metal and ligand (MLCT), since free 2,2'-bpy ligand does not show any luminescence in the range of 400–500 nm. The enhancement and significant blue-shift of the luminescence of 2,2'-bpy ligand may be attributed to its chelation to the metal ion, which effectively increases the rigidity of the 2,2'-bpy ligand [48–49].

The 1H NMR spectra of **2** and **5** show a doublet of doublet at 1.1 ppm ($^3J_{H-H} = 2.2$ and 5.5 Hz) which correspond to the protons of isopropyl methyl groups. As expected, the methine proton of isopropyl group shows a septet and confirms the presence of isopropyl groups. A singlet at 2.3 and 2.4 ppm, respectively, correspond



Scheme 1.

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