



# Supramolecular complexes of Co(II), Ni(II) and Zn(II) *p*-hydroxybenzoates with caffeine: Synthesis, spectral characterization and crystal structure

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## ABSTRACT

Three novel complexes Co(II), Ni(II) and Zn(II) containing *p*-hydroxybenzoates and caffeine ligands were synthesized and characterized by elemental analysis, FT-IR and UV–vis Spectroscopy, molar conductivity and single crystal X-ray diffraction methods. The thermal properties of the synthesized complexes were investigated by TGA/DTA. The general formula of the complexes is  $[M(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4] \cdot 2(\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2) \cdot 8\text{H}_2\text{O}$  (where: M: Co, Ni and Zn). The IR studies showed that carboxylate groups of *p*-hydroxybenzoate ligands have monodentate coordination mode. The  $\text{M}^{2+}$  ions are octahedrally coordinated by two *p*-hydroxybenzoate ligands, four water molecules leading to an overall  $\text{MO}_6$  coordination environment. The medium-strength hydrogen bondings involving the uncoordinated caffeine ligands and water molecules, coordinated and uncoordinated water molecules and *p*-hydroxybenzoate ligands lead to three-dimensional supramolecular networks in the crystal structures.

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## 1. Introduction

Intermolecular interactions, that is to be much weaker than the covalent bonds, play an important role in the formation of complex molecules. These studies led to the formation of a branch known as supramolecular chemistry. Metal-organic supramolecular complexes have attracted considerable attention for their structural diversity and applications [1–7].

Heterocyclic organic ligands that are commonly used with metal arylcarboxylates such as the derivatives of *N*-heterocyclic categories involving caffeine, pyridine and their derivatives, imidazole and 1,10-phenanthroline, are used as linkers and construct a great variety of structure architectures [8–13]. Caffeine that is called 3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione has been known to have attractive effects on various biological systems such as cardiovascular, gastrointestinal, respiratory and muscle systems

[8,14,15]. Its complexes with transition metals have different coordination and biological properties such as antibacterial and anti-inflammatory [15–18]. Transition metal complexes of aromatic carboxylic acid derivatives with *N*- and *O*- donor ligands have wide range of crystal engineering such as metal organic frameworks (MOFs) and supramolecular structures. Metal arylcarboxylates have extensively different coordination modes [19–26]. Our primary ligand, *p*-hydroxybenzoic acid, that is also one of the biologically important compound because a component of *p*-hydroxybenzoic hydroxylases, has been shown various coordination mode such as ionic, monodentate, bidentate chelating, bidentate bridging (symmetric or unsymmetric) [27,28].

In this study, three isomeric complexes, namely  $\text{Co}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4 \cdot (\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2)_2 \cdot 8\text{H}_2\text{O}$  (compound **1**),  $[\text{Ni}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4] \cdot (\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2)_2 \cdot 8\text{H}_2\text{O}$  (compound **2**) and  $[\text{Zn}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4] \cdot (\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2)_2 \cdot 8\text{H}_2\text{O}$  (compound **3**), were reported. The prepared complexes were characterized by elemental analysis, molar conductance, solubility in different solvents and spectral studies (IR and UV–vis). Thermal stabilities of the complexes have been discussed. The crystal structures of the

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complexes were determined by single-crystal XRD method.

## 2. Experimental

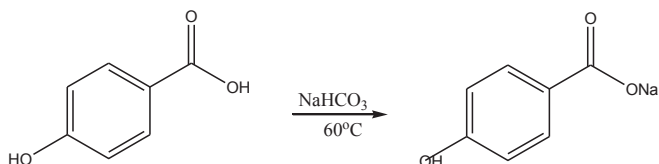
### 2.1. Materials and instrumentation

All chemicals were analytical grade products and used without any purification. Elemental analysis for C, H and N were performed on a LECO, CHNS-932 elemental analyzer, FT-IR Spectra were recorded on Perkin Elmer Frontier™ FT-IR Spectrometer with solid samples using a Diamond ATR accessory in the range of 4000–600  $\text{cm}^{-1}$  (product number: L1280100, TGS detector 11000:1). Resolution was set up to 4  $\text{cm}^{-1}$ , signal/noise ratio was established by 4 scans. UV–Vis Spectra were measured in water ( $10^{-3}$  M) by using Perkin Elmer Lambda 25 spectrometer between 200 and 1000 nm. The thermal properties of the complexes were performed and recorded simultaneously in a static nitrogen atmosphere with the help of Shimadzu DTG 60 Thermal Analyzer (Hacettepe University, Turkey). The experiments were performed in static nitrogen atmosphere with a heating rate of 10  $^{\circ}\text{C min}^{-1}$  from room temperature to 1000  $^{\circ}\text{C}$  in platinum crucibles. The samples were approximately 10 mg and highly sintered  $\alpha\text{-Al}_2\text{O}_3$  was used as a reference material. The DTG sensitivity was 0.05  $\text{mg s}^{-1}$ . Molar conductivity values of the complexes were measured by using COND iSET315 in DMF ( $10^{-3}$  M) in water solutions at room temperature.

Single crystal X-ray diffraction analyses of compound **1**, compound **2** and compound **3** were performed on a Bruker SMART BREEZE CCD diffractometer using Mo  $K_{\alpha}$  ( $\lambda = 0.71073$  Å) radiation at a temperature of 296 K. Structures were solved by direct methods [29] and refined by full-matrix least squares against  $F^2$  using all data. All non-H atoms were refined anisotropically. Atoms H3A (for OH), H41, H42, H51, H52, H81, H82, H91, H92, H101, H102, H111 and H112 (for  $\text{H}_2\text{O}$ ) (in compound **1**, compound **2** and compound **3**) were located in difference Fourier maps and refined isotropically, while the C-bound H atoms were positioned geometrically at distances of 0.93 Å (aromatic CH) and 0.96 Å (for  $\text{CH}_3$ ) (in **1**, **2** and **3**) from the parent C atoms; a riding model was used during the refinement processes and the  $U_{\text{iso}}$  (H) values were constrained to be  $xU_{\text{eq}}$  (carrier atom), where  $x = 1.2$  for aromatic H atoms and  $x = 1.5$  for methyl H atoms. Experimental data are given in Table 1.

#### 2.1.1. Preparation of complexes

**2.1.1.1. Synthesis of  $\text{Co}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4 \cdot (\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2)_2 \cdot 8\text{H}_2\text{O}$  (compound **1**).** For the synthesis of cobalt(II) *p*-hydroxybenzoate with caffeine, firstly sodium salt of *p*-hydroxybenzoate was prepared to the following equation;

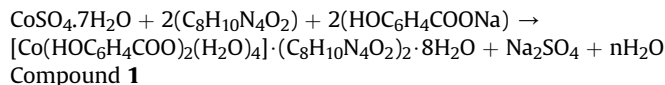


1 mmol of *p*-hydroxybenzoic acid was added to a water solution of 1 mmol  $\text{NaHCO}_3$  (100 mL) and stirred at 60  $^{\circ}\text{C}$  temperature till removed of  $\text{CO}_2$  gas and obtained the sodium *p*-hydroxybenzoate solution.

1 mmol caffeine (100 mL) was added to 100 mL of 0.5 mmol  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  in 25 mL of water. The prepared sodium *p*-hydroxybenzoate solution was added to this solution ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  + caffeine). This solution was left to crystallization at

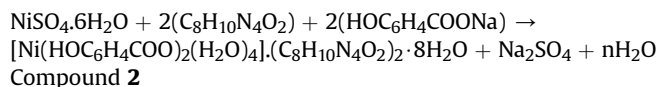
ambient temperature. After two or three weeks, the obtained pink product was filtered off, washed with distilled water and dried in air atmosphere. The obtained all crystals were suitable for single crystal X-ray analysis.

Anal. Calcd. (%) for compound **1**,  $\text{C}_{30}\text{H}_{54}\text{CoN}_8\text{O}_{22}$  (MW = 937.74) C, 38.43; H, 5.80; N, 11.95. Found (%): C, 38.22; H, 6.10; N, 11.95; Selected IR bands ( $\text{cm}^{-1}$ ):  $\nu(\text{OH})_{\text{H}_2\text{O}}$  3387,  $\nu(\text{OH})_{\text{phen}}$  3270,  $\nu(\text{C-H})_{\text{arom}}$  3120,  $\nu(\text{C-H})_{\text{CH}_3}$  2957,  $\nu(\text{C=O})_{\text{caff}}$  1688,  $\nu(\text{C=N})_{\text{caff}}$  1637,  $\nu(\text{COO}^-)_{\text{as}}$  1599,  $\nu(\text{COO}^-)_{\text{s}}$  1382,  $\Delta\nu(\text{COO}^-)$  217,  $\nu(\text{C-C})_{\text{phen}}$  1465,  $\nu(\text{C-OH})_{\text{phen}}$  1237,  $\delta(\text{COO}^-)$  861,  $\delta(\text{C-H})_{\text{phen}}$  743,  $\rho_r(\text{H}_2\text{O})$ , 788  $\rho_w(\text{H}_2\text{O})$  623. UV–Vis [ $\lambda$  (nm)]: 304, 512. Molar Conductivity ( $\mu\text{S/cm}$ ): 3.2.



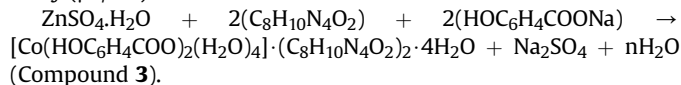
**2.1.1.2. Synthesis of  $\text{Ni}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4 \cdot (\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2)_2 \cdot 8\text{H}_2\text{O}$  (compound **2**).** The preparation of compound **2** followed the same procedure described for  $\text{Co}(\text{HO-C}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4 \cdot (\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2)_2 \cdot 8\text{H}_2\text{O}$ , using a solution of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  in 25 mL of water.

Anal. Calcd. (%) for compound **2**,  $\text{C}_{30}\text{H}_{54}\text{NiN}_8\text{O}_{22}$  (MW = 937.50) C, 38.43; H, 5.81; N, 11.95. Found (%): C, 38.24; H, 6.07; N, 11.97; Selected IR bands ( $\text{cm}^{-1}$ ):  $\nu(\text{OH})_{\text{H}_2\text{O}}$ , 3247  $\nu(\text{OH})_{\text{phen}}$  3247,  $\nu(\text{C-H})_{\text{arom}}$  3118,  $\nu(\text{C-H})_{\text{CH}_3}$  2971,  $\nu(\text{C=O})_{\text{caff}}$  1695,  $\nu(\text{C=N})_{\text{caff}}$  1647,  $\nu(\text{COO}^-)_{\text{as}}$  1597,  $\nu(\text{COO}^-)_{\text{s}}$  1390,  $\Delta\nu(\text{COO}^-)$  207,  $\nu(\text{C-C})_{\text{phen}}$  1450,  $\nu(\text{C-OH})_{\text{phen}}$  1237,  $\delta(\text{COO}^-)$  855,  $\delta(\text{C-H})_{\text{phen}}$  744  $\rho_r(\text{H}_2\text{O})$ , 787  $\rho_w(\text{H}_2\text{O})$  624. UV–Vis [ $\lambda$  (nm)]: 299, 395, 697. Molar Conductivity ( $\mu\text{S/cm}$ ): 4.8.



**2.1.1.3. Synthesis of  $\text{Zn}(\text{HOC}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4 \cdot (\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2)_2 \cdot 8\text{H}_2\text{O}$  (compound **3**).** The preparation of compound **3** followed the same procedure described for  $\text{Co}(\text{HO-C}_6\text{H}_4\text{COO})_2(\text{H}_2\text{O})_4 \cdot (\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2)_2 \cdot 8\text{H}_2\text{O}$ , using a solution of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  in 25 mL of water.

Anal. Calcd. (%) for compound **3**,  $\text{C}_{30}\text{H}_{54}\text{ZnN}_8\text{O}_{22}$  (MW = 944.20): C, 38.16; H, 5.81; N, 12.14. Found (%): C, 38.64; H, 5.60; N, 11.87; Selected IR bands ( $\text{cm}^{-1}$ ):  $\nu(\text{OH})_{\text{H}_2\text{O}}$  3380,  $\nu(\text{OH})_{\text{phen}}$  3267,  $\nu(\text{C-H})_{\text{arom}}$  3116,  $\nu(\text{C-H})_{\text{CH}_3}$  2955,  $\nu(\text{C=O})_{\text{caff}}$  1688,  $\nu(\text{C=N})_{\text{caff}}$  1635,  $\nu(\text{COO}^-)_{\text{as}}$  1599,  $\nu(\text{COO}^-)_{\text{s}}$  1381,  $\Delta\nu(\text{COO}^-)$  218,  $\nu(\text{C-C})_{\text{phen}}$  1465,  $\nu(\text{C-OH})_{\text{phen}}$  1236,  $\delta(\text{COO}^-)$  861,  $\delta(\text{C-H})_{\text{phen}}$  743  $\rho_r(\text{H}_2\text{O})$ , 788  $\rho_w(\text{H}_2\text{O})$  623. UV–Vis [ $\lambda$  (nm)]: 302. Molar Conductivity ( $\mu\text{S/cm}$ ): 3.4.



## 3. Result and discussion

The synthesized complexes were found to be stable at room temperature and insoluble in solvents such as  $\text{CCl}_4$  and  $\text{CHCl}_3$ , weak soluble in EtOH and MeOH, soluble in  $(\text{CH}_3)_2\text{CO}$ , DMSO, DMF and  $\text{H}_2\text{O}$ .

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