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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 $[M(HOC_6H_4COO)_2(H_2O)_4]\cdot 2(C_8H_{10}N_4O_2)\cdot 8H_2O$ (where: M: Co, Ni and Zn). The IR studies showed that carboxylate groups of *p*-hydroxybenzoate ligands have monodentate coordination mode. The M^{2+} ions are octahedrally coordinated by two *p*-hydroxybenzoate ligands, four water molecules leading to an overall 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.

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, pyridyne and their derivates, imidazole and 1,10-phenantroline, 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 derivates 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 primarily ligand, *p*-hydroxybenzoic acid, that is also one of the biologically important compound because a component of *p*-hydroxybenzoic hydroxlases, 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 $Co(HOC_6H_4COO)_2(H_2O)_4]\cdot(C_8H_{10}N_4O_2)_2\cdot 8H_2O$ (compound **1**), $[Ni(HOC_6H_4COO)_2(H_2O)_4]\cdot(C_8H_{10}N_4O_2)_2\cdot 8H_2O$ (compound **2**) and $[Zn(HOC_6H_4COO)_2(H_2O)_4]\cdot(C_8H_{10}N_4O_2)_2\cdot 8H_2O$ (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

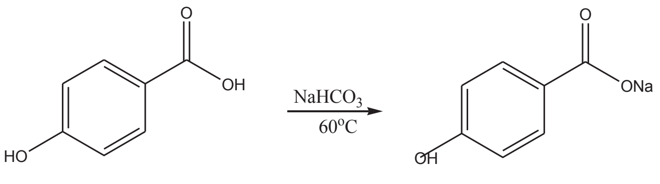
2.1. Materials and instrumentation

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 cm^{-1} (product number:L1280100, TGS detector 11000:1). Resolution was set up to 4 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 Schimadzu DTG 60 Thermal Analyzer (Hacettepe University, Turkey). The experiments were performed in static nitrogen atmosphere with a heating rate of 10 °C min^{-1} from room temperature to 1000 °C in platinum crucibles. The samples were approximately 10 mg and highly sintered α-Al_2O_3 was used as a reference material. The DTG sensitivity was 0.05 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_α ($\lambda = 0.71073$ 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 H_2O) (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 CH_3) (in 1, 2 and 3) from the parent C atoms; a riding model was used during the refinement processes and the U_{iso} (H) values were constrained to be xU_{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 $Co(HOC_6H_4COO)_2(H_2O)_4]\cdot(C_8H_{10}N_4O_2)_2\cdot 8H_2O$ (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 $NaHCO_3$ (100 mL) and stirred at 60 °C temperature till removed of CO_2 gase and obtained the sodium *p*-hydroxybenzoate solution.

1 mmol caffeine (100 mL) was added to 100 mL of 0.5 mmol $CoSO_4\cdot 7H_2O$ in 25 mL of water. The prepared sodium p-hydroxybenzoate solution was added to this solution ($CoSO_4\cdot 7H_2O$ + 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**, $C_{30}H_{54}CoN_8O_{22}$ (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 (cm^{-1}): $\nu(OH)_{H2O}$ 3387, $\nu(OH)_{phen.}$ 3270, $\nu(C{-}H)_{arom.}$ 3120, $\nu(C{-}H)_{CH3}$. 2957, $\nu(C{=}O)_{caff.}$ 1688, $\nu(C{=}N)_{caff.}$ 1637, $\nu(COO^-)_{as}$ 1599, $\nu(COO^-)_s$ 1382, $\Delta\nu(COO^-)$ 217, $\nu(C{-}C)_{phen}$ 1465, . $\nu(C{-}OH)_{phen.}$ 1237, $\delta(COO^-)$ 861, $\delta(C{-}H)_{phen.}$ 743, $\rho_r(H_2O)$, 788 $\rho_w(H_2O)$ 623. UV–Vis [λ (nm),]: 304, 512. Molar Conductivity (μS/cm): 3.2.

$CoSO_4.7H_2O + 2(C_8H_{10}N_4O_2) + 2(HOC_6H_4COONa) \rightarrow$
$[Co(HOC_6H_4COO)_2(H_2O)_4]\cdot(C_8H_{10}N_4O_2)_2\cdot 8H_2O + Na_2SO_4 + nH_2O$
Compound **1**

*2.1.1.2. Synthesis of $Ni(HOC_6H_4COO)_2(H_2O)_4].(C_8H_{10}N_4O_2)_2\cdot 8H_2O$ (compound **2**).* The preparation of compound **2** followed the same procedure described for $Co(HO{-}C_6H_4COO)_2(H_2O)_4]\cdot(C_8H_{10}N_4O_2)_2\cdot 8H_2O$, using a solution of $NiSO_4.6H_2O$ in 25 mL of water.

Anal. Calcd. (%) for compound **2**, $C_{30}H_{54}Ni\ N_8O_{22}$ (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 (cm^{-1}): $\nu(OH)_{H2O}$, 3247$\nu(OH)_{phen}$ 3247., $\nu(C{-}H)_{arom.}$ 3118, $\nu(C{-}H)_{CH3}$. 2971, $\nu(C{=}O)_{caff.}$ 1695, $\nu(C{=}N)_{caff}$ 1647., $\nu(COO^-)_{as}$1597, $\nu(COO^-)_s$1390, $\Delta\nu(COO^-)$ 207, $\nu(C{-}C)_{phen}$ 1450, $\nu(C{-}OH)_{phen.}$ 1237, $\delta(COO^-)$ 855, $\delta(C{-}H)_{phen.}$744 $\rho_r(H_2O)$, 787 $\rho_w(H_2O)$ 624. UV–Vis [λ (nm),]: 299, 395, 697. Molar Conductivity (μS/cm): 4.8.

$NiSO_4.6H_2O + 2(C_8H_{10}N_4O_2) + 2(HOC_6H_4COONa) \rightarrow$
$[Ni(HOC_6H_4COO)_2(H_2O)_4].(C_8H_{10}N_4O_2)_2\cdot 8H_2O + Na_2SO_4 + nH_2O$
Compound **2**

*2.1.1.3. Synthesis of $Zn(HOC_6H_4COO)_2(H_2O)_4]\cdot(C_8H_{10}N_4O_2)_2\cdot 8H_2O$ (compound **3**).* The preparation of compound **3** followed the same procedure described for $Co(HO{-}C_6H_4COO)_2(H_2O)_4]\cdot(C_8H_{10}N_4O_2)_2\cdot 8H_2O$, using a solution of $MnSO_4.H_2O$ in 25 mL of water.

Anal. Calcd. (%) for compound **3**, $C_{30}H_{54}ZnN_8O_{22}$ (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 (cm^{-1}): $\nu(OH)_{H2O}$ 3380, $\nu(OH)_{phen.}$ 3267, $\nu(C{-}H)_{arom.}$ 3116, $\nu(C{-}H)_{CH3}$. 2955, $\nu(C{=}O)_{caff.}$ 1688, $\nu(C{=}N)_{caff.}$ 1635, $\nu(COO^-)_{as}$ 1599, $\nu(COO^-)_s$ 1381, $\Delta\nu(COO^-)$ 218, $\nu(C{-}C)$-$_{phen.}$1465, . $\nu(C{-}OH)_{phen.}$ 1236, $\delta(COO^-)$ 861, $\delta(C{-}H)_{phen.}$ 743 $\rho_r(H_2O)$, 788 $\rho_w(H_2O)$ 623. UV–Vis [λ (nm),]: 302. Molar Conductivity (μS/cm): 3.4.

$ZnSO_4.H_2O + 2(C_8H_{10}N_4O_2) + 2(HOC_6H_4COONa) \rightarrow [Co(HOC_6H_4COO)_2(H_2O)_4]\cdot(C_8H_{10}N_4O_2)_2\cdot 4H_2O + Na_2SO_4 + nH_2O$ (Compound **3**).

3. Result and discussion

The synthesized complexes were found to be stable at room temperature and insoluble in solvents such as CCl_4 and $CHCl_3$, weak soluble in EtOH and MeOH, soluble in $(CH_3)_2CO$, DMSO, DMF and H_2O.

Table 1
Experimental details for compound **1**, compound **2** and compound **3**.

	Compound 1	Compound 2	Compound 3
Empirical Formula	$C_{30}H_{54}Co\ N_8\ O_{22}$	$C_{30}H_{54}N_8NiO_{22}$	$C_{30}H_{54}N_8O_{22}Zn$
Formula weight	937.74	937.50	944.20
Colour/shape	pink/prism	green/prism	colorless/block
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	$P\ 2_1/c$	$P\ 2_1/c$	$P\ 2_1/c$
a (Å)	11.1083(3)	11.0894(3)	11.0851(3)
b (Å)	14.1929(4)	14.1405(4)	14.1911(4)
c (Å)	13.4831(4)	13.4735(4)	13.4709(4)
α (°)	90	90	90
β (°)	101.76(3)	101.767(3)	101.655(3)
γ (°)	90	90	90
V (Å^3)	2081.12(10)	2068.37(10)	2075.41(10)
Z	2	2	2
μ (Mo K_α) (mm^{-1})	0.506	0.563	0.685
ρ (calcd) (mg m^{-3})	1.497	1.505	1.511
Number of Reflections Total	5229	5211	5095
Number of Reflections Unique	4721	4839	3265
R_{int}	0.0318	0.0260	0.1040
$2\theta_{max}$ (°)	56.90	56.96	57.24
T_{min}/T_{max}	0.770/0.900	0.800/0.884	0.745/0.927
Number of Parameters	333	332	332
GOF	1.054	1.066	1.030
R [$F^2 > 2\sigma(F^2)$]	0.0548	0.0508	0.0542
wR	0.1565	1.468	0.1030
$(\Delta\rho)_{max}$ (e Å^{-3})	1.449	1.567	0.688
$(\Delta\rho)_{min}$ (e Å^{-3})	−0.493	−0.511	−0.417

3.1. *Descriptions of the crystal structures*

The X-ray structural determinations of compound **1**, compound **2** and compound **3** confirm the assignments of their structures from spectroscopic data. Selected bond lengths and angles are given in Table 2. Hydrogen bond geometry is given in Table 3. The molecular structures along with the atom-numbering schemes are depicted in Figs. 1–3, while the packing diagrams are given in Figs. 4–6, respectively.

In the mononuclear complexes compound **1**, compound **2** and compound **3**, the metal (Co, Ni and Zn for compound **1**, compound **2** and compound **3**, respectively) atoms are located on inversion centers and coordinated by two *p*-hydroxybenzoate (HB) anions and four water molecules, with all ligands coordinating in a monodentate manner, the asymmetric units of the complexes also contain four uncoordinated water molecules and one caffeine ligand (Figs. 1–3). The four symmetry-related water O atoms (O4, O4^i, O5 and O5^i) form slightly distorted square-planar arrangements, while the slightly distorted octahedral coordination spheres are completed by the two symmetry-related O atoms (O2 and O2^i) of the two carboxylate ligands in the axial positions [symmetry codes: (i) −x, −y, 1 −z (for compounds **1** and compound **2**) and (i) 1 −x, −y, −z (for compound **3**)]. while the intermolecular O–H···O hydrogen bonds (Table 3) link the uncoordinated water molecules to each others, the three uncoordinated water molecules to the coordinated water molecule and *p*-hydroxybenzoate anion, and the *p*-hydroxybenzoate anion to the caffeine ligand (Figs. 1–3).

The very similar C1–O1 and C1–O2 bond lengths (Table 2) of the carboxylate groups indicate delocalized bonding arrangements, rather than localized single and double bonds. The average M–O bond lengths (where M is metal) are 2.0695(17) Å (in compound **1**), 2.0435(15) Å (in compound **2**) and 2.0572(17) Å (in compound **3**) (for benzoate oxygen atoms) and 2.1208 (18) Å (in compound **1**), 2.0801 (17) Å (in compound **2**) and 2.1245 (20) Å (in compound **3**) (for water oxygen atoms) (Table 2). The M atoms lie 0.3428 (1) Å below (in compound **1**), 0.3222 (1) Å below (in compound **2**) and 0.3443 (1) Å below (in compound **3**) the planar (O1/C1/O2) carboxylate groups. The O-M-O bond angles deviate only slightly from ideal values, with average values of 90.00(7)° (in compound **1**), 89.96(7)° (in compound **2**) and 90.00(8)° (in compound **3**), respectively (Table 2). The dihedral angles between the planar carboxylate groups (O1/C1/O2) and the adjacent benzene rings [*A* (C2–C7)] are 0.19(16)° (in compound **1**), 0.65(19)° (in compound **2**) and 0.63(22)° (in compound **3**), so they are almost coplanar. The caffeine ring systems *D* (N1–N4/C8–C12) are planar with maximum deviations of 0.0233(22) Å (for N3, in compound **1**), 0.0257(21) Å (for N3, in compound **2**) and 0.0226(24) (for N3, in compound **3**), and they are oriented with respect to the benzene rings at dihedral angles of A/D = 1.84(6)° (in compound **1**), A/D = 1.92(6)° (in compound **2**) and A/D = 1.81(7)° (in compound **3**). In compounds **1**, **2** and **3**, **t**he medium-strength intramolecular $O\text{-}H_W\cdots O_{car}$ (car = carboxylate) hydrogen bonds (Table 3) link the coordinated water molecules to the carboxylate oxygen atoms (Figs. 1–3).

In the crystal structures of compounds **1**, **2** and **3**, the medium-

Table 2
Selected bond lengths (Å) and angles (°) for compound **1**, compound **2** and compound **3**.

	Compound 1	Compound 2	Compound 3
M-O2	2.0695(17)	2.0435(15)	2.0572(17)
M-O4	2.1139(18)	2.0855(17)	2.134(2)
M-O5	2.1277(18)	2.0747(16)	2.115(2)
O1–C1	1.263(3)	1.265(3)	1.257(3)
O2–C1	1.258(3)	1.256(3)	1.259(3)
O3–C5	1.365(3)	1.363(3)	1.365(3)
O6–C11	1.224(3)	1.226(3)	1.219(3)
O7–C12	1.246(3)	1.248(3)	1.238(3)
O2-M-O4	88.09(7)	88.58(7)	88.45(8)
O2-M-O4^i	91.91(7)	91.42(7)	91.55(8)
O2-M-O5	92.78(7)	92.70(7)	92.42(8)
O2-M-O5^i	87.22(7)	87.30(7)	87.58(8)
O4-M-O5	91.96(8)	92.64(7)	92.59(9)
O4-M-O5^i	88.04(8)	87.36(7)	87.41(9)
O1–C1–O2	124.1(2)	124.3(2)	124.0(2)

Symmetry codes: (i) − x, − y, 1 − z (for **1** and **2**), (ii) 1 − x, − y, − z (for **3**). M is Co, Ni and Zn for compound **1**, compound **2** and compound **3**, respectively.

Table 3
Hydrogen-bond geometry (Å, °).

	D-h···a	D-H	H···A	D···A	D-h···a
Compound **1**	O3—H3A···O7	0.80(6)	1.97(6)	2.766 (3)	173(5)
	O4—H41···O8	0.81(3)	2.01(3)	2.809 (3)	168(3)
	O4—H42···N2^{i}	0.93(3)	1.95(3)	2.863 (3)	169(3)
	O5—H51···O6^{ii}	0.90(2)	1.93(2)	2.804 (3)	162(2)
	O5—H52···O1	0.83(3)	1.83(2)	2.596 (3)	155(3)
	O8—H81···O11^{iii}	0.948(19)	1.713(19)	2.660 (4)	178(3)
	O8—H82···O3^{iv}	0.81(2)	2.09(3)	2.854 (3)	158(4)
	O9—H91···O8^{v}	0.84(4)	2.00(4)	2.838(4)	171(4)
	O9—H92···O1	0.96(3)	1.73(3)	2.695(3)	177(3)
	O10—H10···O9^{ii}	0.84(3)	2.00(3)	2.830(4)	169(5)
	O10—H102···O9	0.94(4)	1.93(5)	2.860(4)	171(5)
	O11—H111···O10^{vi}	0.81(3)	1.91(3)	2.712(4)	172(3)
	O11—H112···O5	0.90(5)	2.01(4)	2.867(4)	158(5)
Compound **2**	O3—H3A···O7	0.85(2)	1.92(2)	2.771(3)	173(5)
	O4—H41···N2^{i}	0.92(3)	1.97(3)	2.875(3)	166(2)
	O4—H42···O8	0.80(3)	2.03(3)	2.816(3)	167(3)
	O5—H51···O1	0.92(3)	1.73(3)	2.574(2)	153(3)
	O5—H52···O6^{ii}	0.82(3)	2.04(2)	2.816(3)	158(2)
	O8—H81···O11^{iv}	0.96(2)	1.705(19)	2.660(3)	175(4)
	O8—H82···O3^{v}	0.82(3)	2.12(4)	2.856(3)	149(5)
	O9—H91···O1	0.93(3)	1.78(3)	2.700(3)	173(4)
	O9—H92···O8^{iii}	0.83(4)	2.01(4)	2.836(3)	171(5)
	O10—H101···O9	0.93(4)	1.94(4)	2.857(4)	169(5)
	O10—H102···O9^{ii}	0.85(3)	1.99(3)	2.831(4)	171(5)
	O11—H111···O10^{vi}	0.90(3)	1.83(3)	2.712(4)	172(3)
	O11—H112···O5	0.80(5)	2.10(4)	2.876(3)	158(5)
Compound **3**	O3—H3A···O7	0.83(2)	1.94(2)	2.772(3)	175(4)
	O4—H41···N2^{i}	0.90(3)	1.97(3)	2.853(3)	168(2)
	O4—H42···O8	0.78(3)	2.07(3)	2.822(3)	163(3)
	O5—H51···O1	0.83(3)	1.83(3)	2.586(3)	150(3)
	O5—H52···O6^{ii}	0.90(2)	1.92(2)	2.807(3)	168(2)
	O8—H81···O11^{iii}	0.82(2)	1.84(2)	2.662(4)	180(4)
	O8—H82···O3^{iv}	0.89(3)	2.02(3)	2.843(3)	154(4)
	O9—H91···O1	0.95(3)	1.76(3)	2.695(3)	167(4)
	O9—H92···O8^{v}	0.85(4)	1.99(4)	2.831(4)	167(3)
	O10—H101···O9	0.82(3)	2.04(4)	2.855(4)	172(4)
	O10—H102···O9^{ii}	0.96(3)	1.86(3)	2.819(4)	170(4)
	O11—H111···O10^{vi}	0.81(3)	1.90(3)	2.701(4)	172(3)
	O11—H112···O5	0.88(3)	2.03(3)	2.869(3)	159(4)

Symmetry codes: [(i) −x−1, −y+1, −z+1; (ii) −x, −y+1, −z+1; (iii) x, −y+1/2, z+1/2; (iv) x+1, −y+1/2, z+1/2; (v) x, −y+1/2, z−1/2; (vi) −x, y−1/2, −z+1/2 (for **1**)], [(i) −x−1, −y+1, −z+1; (ii) −x, −y+1, −z+1; (iii) x, −y+1/2, z−1/2; (iv) x, −y+1/2, z+1/2; (v) x+1, −y+1/2, z+1/2; (vi) −x, y−1/2, −z+1/2 (for **2**)] and [(i) −x, −y+1, −z; (ii) −x+1, −y+1, −z; (iii) x, −y+1/2, z+1/2; (iv) x+1, −y+1/2, z+1/2; (v) x, −y+1/2, z−1/2; (vi) −x+1, y−1/2, −z−1/2 (for **3**)].

strength O—H$_{OH}$···O$_{caf}$ (caf = caffeine), O—H$_{w}$···O$_{w}$ (w = water), O—H$_{w}$···N$_{caf}$, O—H$_{w}$···O$_{caf}$ and O—H$_{w}$···O$_{car}$ (car = carboxylate) hydrogen bonds (Table 3) link the molecules into three-dimensional supramolecular networks (Figs. 3–5). The π···π interactions between the benzene [*A* (C2—C7)] and caffeine [*B* (N1/N2/C8—C10) and *C* (N3/N4/C9—C12)] rings, Cg2— Cg1, Cg2— Cg1^{i}, Cg3— Cg1 and Cg3— Cg1^{i} [symmetry code: (i) x, ½ - y, z − ½, where Cg1, Cg2 and Cg3 are the centroids of the rings *A* (C2—C7), *B* (N1/N2/C8—C10) and *C* (N3/N4/C9—C12), respectively] may stabilize the structures with the centroid—centroid distances of 3.627(2) Å, 3.668(2) Å, 3.560(1) Å and 3.495(1) Å (in compound **1**), 3.618(1) Å, 3.659(1) Å, 3.561(1) Å and 3.500(1) Å (in compound **2**) and 3.615(2) Å, 3.658(2) Å, 3.563(2) Å and 3.490(2) Å (in compound **3**).

3.2. Spectral properties and molar conductivity

FT-IR spectra of the complexes have been given in supplementary material file (Suppl. Fig. 1–4). The absorption bands are recorded in the range of 3400–3200 cm^{-1} due to coordination and lattice water molecules. The strecting frequency of phenolic C—OH of the *p*-hydroxybenzoic acid is showed around 1250 cm^{-1} and this peak remained almost in the same position in all synthesized complexes [30]. The strecting frequencies of phenolic OH and phenolic C—OH are observed at 3200 and 1250 cm^{-1}, respectively. This confirms that phenolic OH is not involved in coordination. Δυ(COO^{-}) value gives information about coordination mode of the carboxylate groups. This value is calculated from difference of assymmetric and symmetric streching frequencies of carboxylate group bands. The coordination type of carboxylate groups of *p*-hydroxybenzoate ligands is determined as monodentate from calculated Δυ(COO^{-}) values. Because the obtained Δυ(COO^{-}) values are higher than the Δυ(COO^{-}) value (131 cm^{-1}) of sodium *p*-hydroxybenzoate salt [31,32]. For all complexes, a number of characteristic absorption bands of caffeine are observed at *ca.* 2950, 1680 and 1630 cm^{-1} due to ν(C—H)$_{CH3}$, ν(C═O), ν(C═N), respectively. These frequencies are similar to those of all synthesized complexes [33]. For compound **1**, compound **2** and compound **3**, the

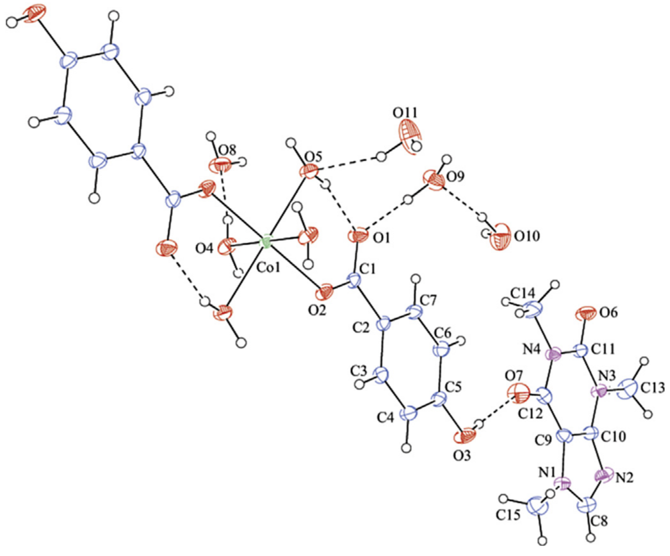


Fig. 1. An ORTEP-3 [43] view of Compound **1**. The thermal ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

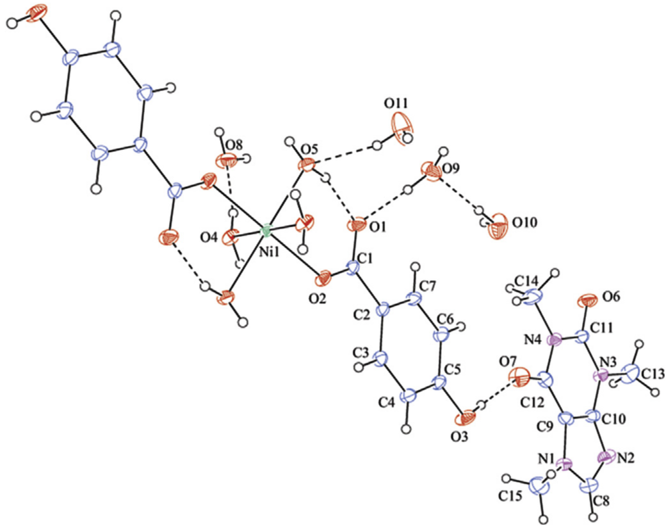


Fig. 2. An ORTEP-3 [43] view of Compound **2**. The thermal ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

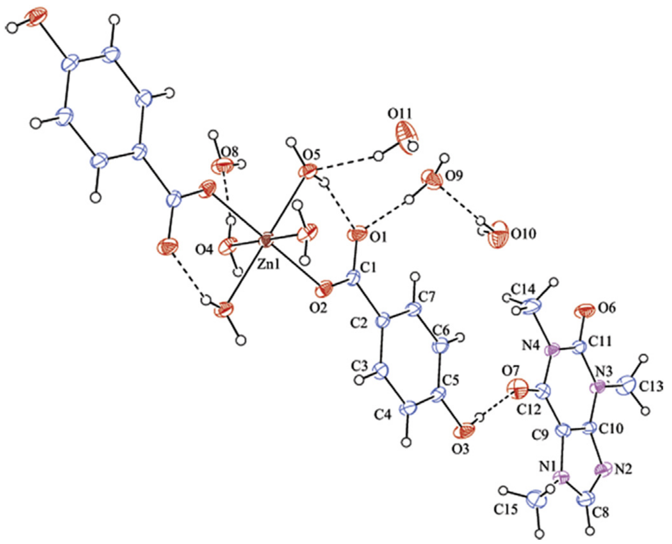


Fig. 3. An ORTEP-3 [43] view of Compound **3**. The thermal ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

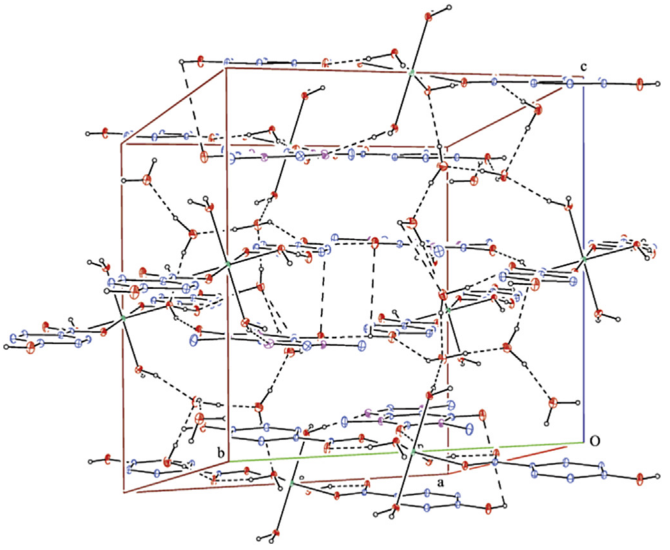


Fig. 4. A partial packing diagram of Compound **1**. Hydrogen bonds are shown as dashed lines. Non-bonding H atoms have been omitted for clarity.

$\rho_r(H_2O)$ and $\rho_\omega(H_2O)$ bands in the spectra of the complexes are observed at 788, 787, 788 and 623, 624, 623 cm^{-1}, respectively, indicates the presence of coordinated water [34].

Electronic absorption spectra of complexes were recorded by using 10^{-3} M solutions of the complexes in water solutions (Suppl. Fig. 5–7). All three complexes showed a strong absorption band between 290 and 310 nm. These are assigned to intraligand $\pi-\pi^*$ transitions in the complexes. The electronic spectrum of compound **1** shows a absorption band at 512 nm. This is assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}$ (P) transition, characteristic of an octahedral geometry. The compound **2** exhibited two bands at 697 and 395 nm attributed to the $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transitions, respectively, indicating an octahedral geometry around the Ni(II) center. Compound **3** as expected, didn't show any peak for *d*–*d* transitions. The observed absorption bands of prepared complexes are in good accordance with literature [35,36].

Molar conductance values of the synthesized complexes are in the range 3.2–4.8 μS/cm in DMF, indicating non-electrolyte and neutral behaviors of them, because the molar conductance values of synthesized complexes are more less than the values of 1:1 electrolyte type [37].

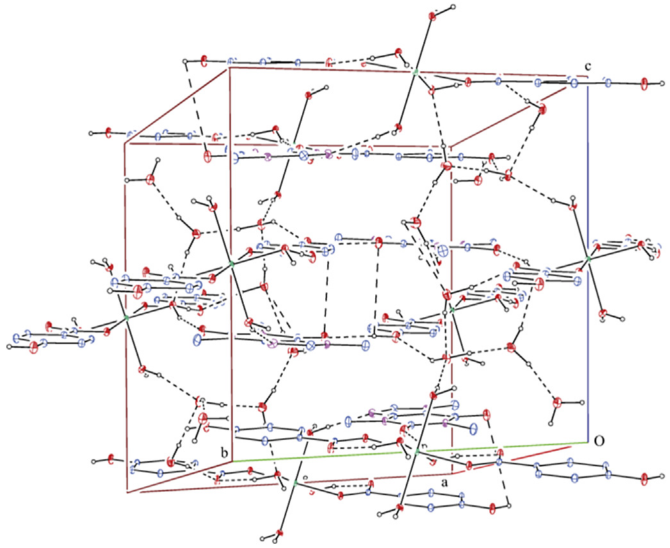


Fig. 5. A partial packing diagram of Compound **2**. Hydrogen bonds are shown as dashed lines. Non-bonding H atoms have been omitted for clarity.

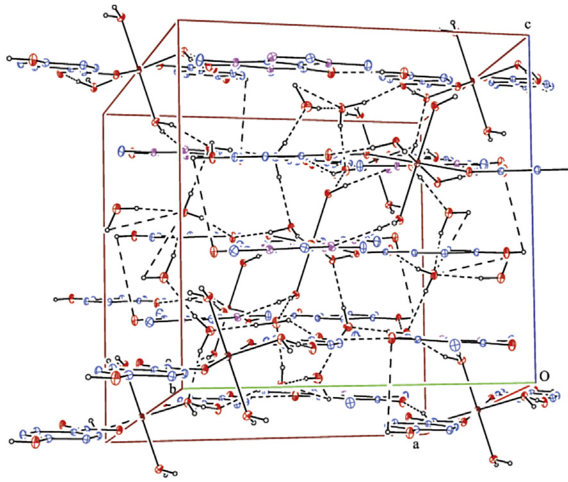


Fig. 6. A partial packing diagram of Compound **3**. Hydrogen bonds are shown as dashed lines. Non-bonding H atoms have been omitted for clarity.

3.3. Thermal analysis

Figures of all complexes related to thermal analysis have been given in supplementary material file (Suppl. Figs. 8–10). Complexes are stable up to about 60 °C. The TGA curves of all complexes shows an initial weight loss which corresponds to the removal of lattice and coordinated water (exp. 22.26%, calc. 23.05% for compound **1**; 22.49% calc. 23.06% for compound **2**; exp. 22.36% calc. 22.88% for compound **3**). According to the literature, the loss of lattice water molecules is taken place in the temperature range 50–150 °C and those of the coordination water molecules is taken place over 150 °C [38,39]. The loss of all water molecules from our synthesized complex molecules continues up to 190, 190 and 245 °C, respectively (for compounds **1**, compound **2** and compound **3**). After the dehydration steps, as can be seen in literature [40–42], caffeine molecules are released from the complexes. For compounds **1** and compound **3**, two molecules caffeine are released in the temperature range 190–390 °C and 245–305 °C with endothermic effect on the DTA curve at 324 °C and 306 °C, respectively. (exp. 54.92%, calc. 53.79% for compound **1**; exp. 52.06% calc. 53.29% for compound **3**). For compound **2**, two molecules caffeine are gradually released in the temperature range 190–275 °C and 275–355 °C and 355–395 °C with depicted as endothermic effect on the DTA curve at 307 °C (exp. 51.93%, calc. 53.79% for compound **2**). The final products of the thermal decomposition for compound **1**, compound **2** and compound **3** are CoO, NiO and ZnO, respectively (exp. 8.22%, calc. 7.98% for compound **1**; exp. 7.58%, calc. 7.96% for compound **2** and exp. 7.88%, calc. 8.61% for compound **3**).

4. Conclusions

Supramolecular complexes of Co(II), Ni(II) and Zn(II) with p-hydroxybenzoate and caffeine have been prepared and characterized. The M(II) cation of the all synthesized complexes, located on an inversion center, is coordinated by two carboxylate O atoms and four water molecules O atoms within a slightly distorted MO_6 octahedron. The asymmetric unit of the mononuclear complexes comprises one $M(HOC_6H_4COO)_2(H_2O)_4$ moiety, one caffeine and four water molecules. One non-coordinating caffeine ligand and four water molecules are embedded, which are hydrogen bonded into chains. In the crystal structures of complexes, $O—H_{OH}\cdots O_{caf}$, $O—H_{w}\cdots O_{w}$, $O—H_{w}\cdots N_{caf}$, $O—H_{w}\cdots O_{caf}$ and $O—H_{w}\cdots O_{car}$ hydrogen bonds link the molecules into three-dimensional supramolecular structure.

Appendix A. Supplementary Data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 1418041–1418043 Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44-1223-336033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2016.05.006.

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