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# Mixed ligand complexes of coumarilic acid/nicotinamide with transition metal complexes

## Synthesis and structural investigation

Dursun Ali Köse · Banu Öztürk · Onur Şahin ·  
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**Abstract** Coumarilate–nicotinamide complexes of  $\text{Co}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$  were synthesized and investigated by elemental analysis, magnetic susceptibility, solid state UV–Vis, direct injection probe mass spectra, FTIR spectra, thermoanalytic TG-DTG/DTA, and crystal X-ray diffraction methods. It was obtained that both complex structures contain 2 mol aqua ligands, 2 mol coumarilate ( $\text{CCA}^-$ ) and 2 mol nicotinamide (NA) ligands per formula unit. The  $\text{CCA}^-$  and NA ligands were bonded to metal cations as monodentate through acidic oxygen and nitrogen of pyridine ring, respectively. Thermal decomposition of each complex starts with dehydration and continue removing of 1 mol NA ligand. The thermal dehydration of the complexes takes place in one or two steps. The decomposition mechanism and thermal stability of the investigated complexes are interpreted in terms of their structures. The final decomposition products are found to be metal oxides.

**Keywords** Coumarilic acid · Nicotinamide · Benzo[b]furancarboxylic acid · Metal complexes · Crystal structure · Coumarine derivatives

## Introduction

Coumarin and its derivatives are well-known natural compounds found to be present in different food sources such as fruits, herbs and vegetables [1]. They have used different applications in medicine drugs as spasmolytics, anticoagulants [2], biological inhibitors [3] anticancer [4], antibacterial [5] and antifungal [6]. Today lots of natural or synthetic derivatives have found pharmaceutical applications [7, 8]. Their coordination properties are interesting so, their metal complex structures have been investigated and discussed [9–11]. Their coordination properties have been shown to increase the biological activity [12–15]. The coumarin and its derivatives very important ligands for coordination chemistry, consequently lots of researchers investigated their structural and biologic properties of metal ion complexes [16–18]. But, for a number of these complexes, the isolation of crystals suitable for X-ray analysis often remained unsuccessful, and hence their coordination modes were proposed based on experimental data other than X-ray diffraction [11, 19, 20]. The coumarilic acid has been studied as a ligand in complexation reactions with  $\text{Cu}^{\text{II}}$  [8],  $\text{Sn}^{\text{II}}$  [21],  $\text{Dy}^{\text{III}}$ ,  $\text{Er}^{\text{III}}$ ,  $\text{Eu}^{\text{III}}$ ,  $\text{Gd}^{\text{III}}$ ,  $\text{Tb}^{\text{III}}$ ,  $\text{Sm}^{\text{III}}$  [22, 23],  $\text{La}^{\text{III}}$  [19],  $\text{Ce}^{\text{III}}$ ,  $\text{Nd}^{\text{III}}$  [20],  $\text{Pr}^{\text{III}}$  [24],  $\text{Ni}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$  [11]. Although there are many literature data about metal ions–coumarilic acid complexes, the mixed ligand studies of coumarilic acid with metal ions are very rare.

The reaction conditions and type of the metal ions are very important for different modes of binding of the deprotonated ligand. In the Cu and Sn complexes, the deprotonated carboxylic group acts as a bidentate chelating ligand or as a monodentate-bridged ligand [8, 21, 25]. Another bidentate type of coordination of coumarilate anion was suggested for some lanthanide group metal ion complexes, namely through the oxygen atom of the carbonylic group and the oxygen

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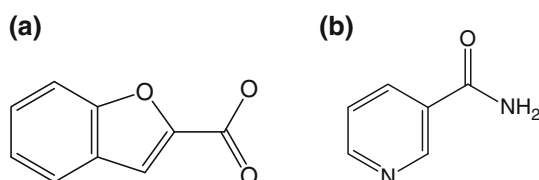
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atom of the deprotonated carboxylic group [22, 23, 26]. The suggestion has been based on spectroscopic data for coumarilic acid ligand (or its potassium salt) and the corresponding metal complexes ( $\Delta = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$ ) [8, 21, 25]. The  $\Delta$  criterion should be used carefully for prediction of the carboxylate group binding type [27–33].

In this paper, we have synthesized of coumarilic acid (coumarin-3-carboxylic acid, benzo[*b*]furan carboxylic acid, HCCA)-nicotinamide (niacin, Vit. B3, NA) (Scheme 1a, b) mixed ligand complexes with  $\text{Zn}^{\text{II}}$  (**I**) and  $\text{Co}^{\text{II}}$  (**II**) metal cations. We then investigated their structural properties by single X-ray diffraction and spectroscopy (UV–Vis, FTIR and mass analysis) and thermal behaviours (TG-DTG/DTA).

## Materials and methods

All chemicals were obtained from Sigma-Aldrich and used without purification. Elemental analysis (C, H, N) were carried out by standard methods (Tubitak Marmara Research Center). Magnetic susceptibility measurements were performed at room temperature using a Sherwood Scientific MXI model Gouy magnetic balance. IR spectra were recorded in the 4000–400  $\text{cm}^{-1}$  region with a Perkin Elmer Spectrum One FTIR spectrophotometer using KBr pellets. Thermal analyses (TG, DTA) were performed by the Shimadzu DTG-60H system, in dynamic nitrogen atmosphere ( $100 \text{ mL min}^{-1}$ ) at a heating rate of  $10 \text{ }^{\circ}\text{C min}^{-1}$ , in platinum crucibles as sample vessel, using  $\alpha\text{-Al}_2\text{O}_3$  as reference.



**Scheme 1** Structure of ligands. **a** Coumarilic acid, **b** Nicotinamide

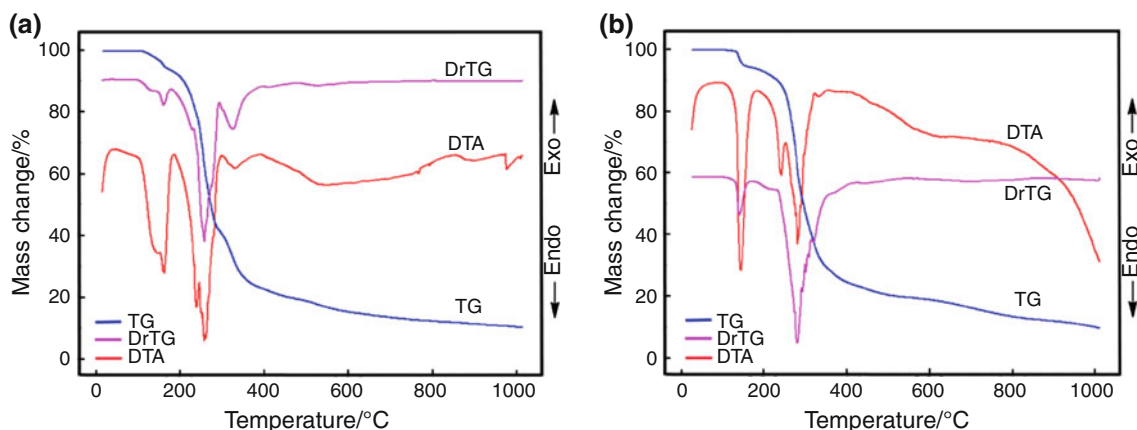
Electronic spectra was recorded by a Shimadzu 3600/UV–Vis–NIR Spectrophotometer. Mass spectrum were recorded Thermo Scientific DSQ II Single Quadrupole GC/MS in the electron impact (EI) ionisation mode (70 eV) and HP-5MS (bonded and cross-linked 5 % phenyl-methylpolysiloxane, 30 mm  $\times$  0.25 mm, coating thickness 0.25  $\mu\text{m}$ ) capillary column (Restek, Bellefonte, PA).

## Synthesis of metal–coumarilate ( $\text{CCA}^-$ )-nicotinamide (NA) complexes

In the first step, sodium salt of coumarilic acid ( $\text{C}_9\text{H}_6\text{O}_3$ ) was prepared at room temperature according to the following equation. All the reactions were carried out in water media.

**Table 1** Some important FT-IR bands of complexes

Groups	$\text{Co}^{\text{II}}$	$\text{Zn}^{\text{II}}$
$\nu(\text{OH})_{\text{H}_2\text{O}}$	3,550–2,900	3,550–2,900
$\nu(\text{NH}_2)$	3,438	3,437
$\nu(\text{NH}_2)_{\text{bending}}$	1,553	1,554
$\nu(\text{C}=\text{O})_{\text{carbonyl}}$	1,669	1,670
$\nu(\text{COO}^-)_{\text{sym}}$	1,597	1,598
$\nu(\text{COO}^-)_{\text{asym}}$	1,397	1,396
$\Delta\nu_{\text{as-s}}$	200	202
$\nu(\text{CH}_2)$	2,807	2,803
$\delta(\text{OH})_{\text{H}_2\text{O}}$	1,472	1,473
$\nu(\text{C}-\text{N}-\text{C})_{\text{pyridine}}$	1,447	1,446
$\nu(\text{C}_9-\text{O}_1-\text{C}_1)$	1,240/1,179	1,240/1,179
$\nu(\text{C}-\text{O})_{\text{carboxyl}}$	1,305	1,303
$\nu(\text{CC}) + \delta(\text{CCH})_{\text{ring}}$	1,333	1,334
$\nu(\text{Ring})$	1,048–820	1,049–818
$\nu(\text{C}-\text{N})_{\text{NA}}$	741–912	724–905
$\nu(\text{M}-\text{N})$	636	637
$\nu(\text{M}-\text{O})$	506	504

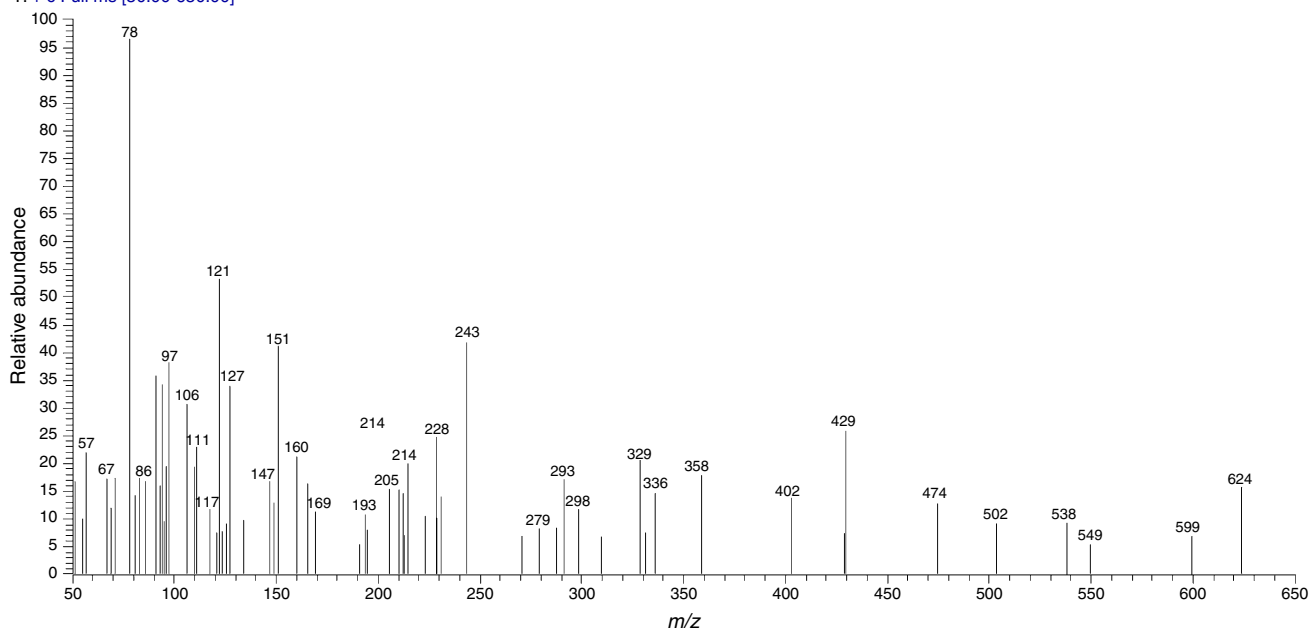


**Fig. 1** Thermal analysis curves of complexes. **a**  $\text{Co}^{\text{II}}$ , **b**  $\text{Zn}^{\text{II}}$

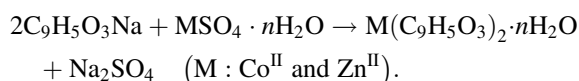
**Table 2** Thermoanalytical results (TG-DTG/DTA) for the metal complexes

Complex	Temperature range/°C	DTA <sub>max</sub> /°C	Removed group	Mass change/%		Total loss/%		Decom. prod.	Colour
				Found	Calc.	Found	Calc.		
[Co(C <sub>9</sub> H <sub>5</sub> O <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O)(H <sub>2</sub> O) <sub>2</sub> ]									Purple
1	123–158	148	H <sub>2</sub> O	2.72	2.69				
2	159–194	181	H <sub>2</sub> O	2.76	2.69				
3	195–261	252	C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O	18.25	18.44				
4	262–303	272	C <sub>9</sub> H <sub>5</sub> O <sub>3</sub> + CONH <sub>2</sub>	31.07	30.99				
5	304–351	341	C <sub>5</sub> H <sub>4</sub> N	11.51	11.79				
6	353–990	553	C <sub>9</sub> H <sub>5</sub> O <sub>3</sub>	23.72	24.34	12.59	11.33	CoO	Black
[Zn(C <sub>9</sub> H <sub>5</sub> O <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O)(H <sub>2</sub> O) <sub>2</sub> ]									White
1	102–164	145	2H <sub>2</sub> O	5.27	5.39				
2	166–267	243	C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O	18.69	18.26				
3	269–298	281	C <sub>9</sub> H <sub>5</sub> O <sub>3</sub>	24.72	24.10				
4	299–341	331	C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O	18.36	18.26				
5	343–991	597	C <sub>9</sub> H <sub>5</sub> O <sub>3</sub>	23.21	24.10	12.98	12.18	ZnO	Black

co(cou)(na)2 #1 RT: 0.04 AV: 1 NL: 9.29E2  
T: + c Full ms [50.00-650.00]

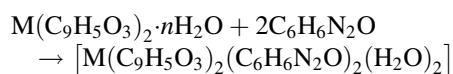
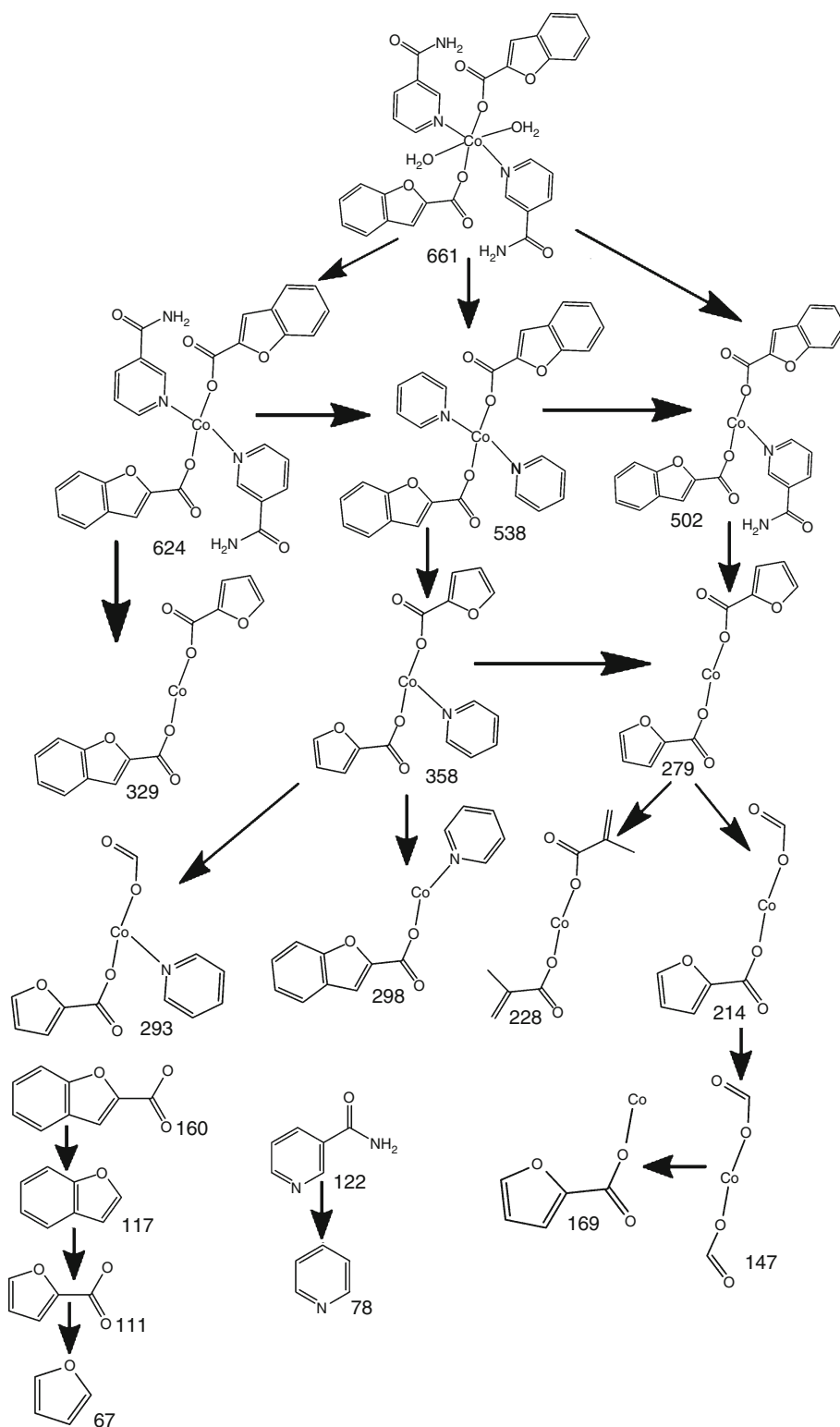
**Fig. 2** Mass spectrum of [Co(CCA)<sub>2</sub>(Na)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complex

In the second step, metal-coumarilate salts were synthesized from Na-coumarilate salt by the following substitution reaction:



Finally, the solution of nicotinamide (2 mmol) in distilled water (30 mL) was added dropwise to a stirred solution of M(CCA)<sub>2</sub>·nH<sub>2</sub>O (1 mmol) in hot distilled water (50 mL). The resulting solution was left 20–22 days for crystallization at room temperature. The crystals formed were filtered and washed with cold water and acetone and dried in vacuum. The mixed ligand metal complexes were prepared according to the following equations:

**Scheme 2** Mass spectral fragmentation pattern of the  $[\text{Co}(\text{CCA})_2(\text{NA})_2(\text{H}_2\text{O})_2]$



The yield of compounds are about 89 % for  $\text{Co}^{\text{II}}$  complex and 92 % for  $\text{Zn}^{\text{II}}$  complex.

Calc. for  $\text{C}_{30}\text{H}_{26}\text{CoN}_4\text{O}_{10}$ : C, 54.42; H, 3.93; N, 8.47.  
Found: C, 54.62; H, 3.38; N, 8.41.

Calc. for  $\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_{10}\text{Zn}$ : C, 53.90; H, 3.89; N, 8.38.  
Found: C, 53.64; H, 4.07; N, 8.27.

## Results and discussion

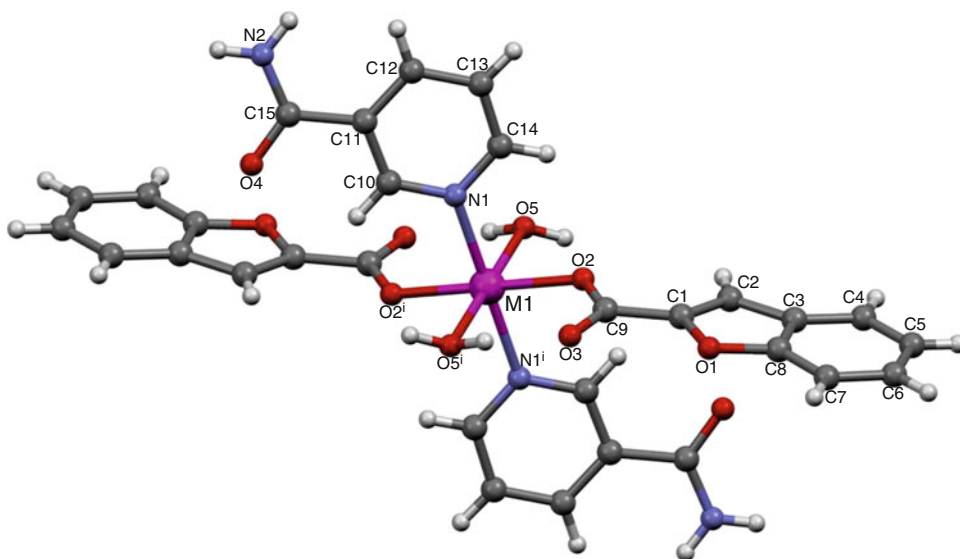
### Electronic spectra

The Bohr magneton data of complexes (3.72 for  $\text{Co}^{\text{II}}$  and diamagnetic for  $\text{Zn}^{\text{II}}$ ) are agreement with literature values for similar complexes [31–33]. According to elemental analysis results, complexes contain two molecules of monoanionic—monodentate coumarilate ( $\text{CCA}^-$ ) and

**Table 3** Crystal data and structure refinement parameters for complexes **I** and **II**

Crystal data	<b>I</b>	<b>II</b>
Empirical formula	$\text{C}_{30}\text{H}_{26}\text{CoN}_4\text{O}_{10}$	$\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_{10}\text{Zn}$
Formula mass	661.48	667.92
Crystal system	Monoclinic	Monoclinic
Space group	$\text{P2}_1/\text{c}$	$\text{P2}_1/\text{c}$
$a/\text{\AA}$	8.8956(4)	8.9265(6)
$b/\text{\AA}$	14.9845(7)	15.0011(9)
$c/\text{\AA}$	13.0733(7)	13.112(1)
$\beta/^\circ$	125.143(3)	124.975(5)
$V/\text{\AA}^3$	1424.97(12)	1438.70(19)
$Z$	2	2
$D_c/\text{g cm}^{-3}$	1.542	1.542
$\mu/\text{mm}^{-1}$	0.67	0.92
$\theta$ Range/ $^\circ$	1.9–28.0	1.9–28.0
Measured refls.	12,855	7,771
Independent refls.	2,956	2,937
$R_{\text{int}}$	0.050	0.037
$S$	1.06	1.05
$R1/wR2$	0.026/0.067	0.028/0.077
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}/\text{e}\text{\AA}^{-3}$	0.28/–0.18	0.26/–0.31

**Fig. 3** The molecular structure of **I** and **II** showing the atom numbering scheme (M1:  $\text{Co}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$ ). ((i)  $-x + 1, -y + 1, -z + 1$ )



neutral—monodentate nicotinamide (NA) ligands per mole formula unit. All of the complexes contain 2 mol of aqua ligands that are directly coordinated to metal ions. Both complexes have octahedral geometry with metal coordinated to two carboxylic oxygen atoms from  $\text{CCA}^-$  and two amine nitrogen atoms from NA and two aqua oxygen atoms. Octahedral structure is confirmed by magnetic data.

The electronic spectra showed two absorption bands attributed to  $d-d$  transitions at  $17,356\text{ cm}^{-1}$  ( ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$ ) (F) and  $21,674\text{ cm}^{-1}$  ( ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}$ )(P) and for  $\text{Co}^{\text{II}}$  complex. According to the magnetic susceptibility results, the  $\text{Zn}^{\text{II}}$  complexes are diamagnetic as expected so no peak was observed for  $d-d$  transitions. The high intensity peaks were detected at  $27,995\text{ cm}^{-1}$  for  $\text{Co}^{\text{II}}$  complex and  $28,569\text{ cm}^{-1}$  for  $\text{Zn}^{\text{II}}$  complex. These peaks are attributed to the metal  $\rightarrow$  ligand charge transfer bands for  $\text{Co}^{\text{II}}$  complex while it is the ligand  $\rightarrow$  metal charge transfer for  $\text{Zn}^{\text{II}}$  complex. The results are agreeable to the literature [31–33].

### Infrared spectra

Some important band values of complexes were summarized in Table 1. The absorption bands observed in the range of  $3,550\text{--}2,900\text{ cm}^{-1}$  correspond to the asymmetric and symmetric stretching vibrations of water molecules. The bands for the N–H stretches of primary amides are strong in the range of  $3438, 3437\text{ cm}^{-1}$ . The N–H bending vibrations appear approximately in the range of  $1,553\text{ cm}^{-1}$ . Normally, the carboxylate complexes give rise to strong bands responsible from the C=O stretching for which conjugation between the carbonyl group and the amide nitrogen causes small frequency shifts [28]. The strong bands observed around  $1,670\text{ cm}^{-1}$  are assigned to

**Table 4** Selected bond distances and angles for complexes **I** and **II** (Å/°)

$C_{30}H_{26}CoN_4O_{10}$					
Co1–N1	2.1086(11)	Co1–O2	2.0589(10)	Co1–O5	2.0739(10)
O2–Co1–O5 <sup>i</sup>	91.91(4)	O2–Co1–O5	88.09(4)	O2–Co1–N1 <sup>i</sup>	88.82(4)
O2–Co1–N1	91.18(4)	O5 <sup>i</sup> –Co1–N1	91.80(5)	O5–Co1–N1	88.20(5)
$C_{30}H_{26}N_4O_{10}Zn$					
Zn1–N1	2.1701(13)	Zn1–O2	2.0947(12)	Zn1–O5	2.1151(12)
O2–Zn1–N1 <sup>i</sup>	91.22(5)	O2–Zn1–N1	88.78(5)	O5–Zn1–N1	91.57(5)
O2–Zn1–O5 <sup>i</sup>	91.16(5)	O2–Zn1–O5	88.84(5)	O5–Zn1–N1 <sup>i</sup>	88.43(5)

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$  for **I**; (i)  $-x + 1, -y + 1, -z + 1$  for **II**

**Table 5** Hydrogen-bonds parameters for complexes **I** and **II** (Å/°)

D–H...A	D–H	H...A	D...A	D–H...A
$C_{30}H_{26}CoN_4O_{10}$				
N2–H2A...O5 <sup>iii</sup>	0.86	2.55	3.1679(18)	129
N2–H2B...O3 <sup>ii</sup>	0.86	2.01	2.8195(19)	157
O5–H5A...O4 <sup>iv</sup>	0.89(2)	1.77(2)	2.6569(15)	172(2)
O5–H5B...O3 <sup>i</sup>	0.89(2)	1.78(2)	2.6298(16)	159(2)
$C_{30}H_{26}N_4O_{10}Zn$				
N2–H2A...O5 <sup>iii</sup>	0.86	2.53	3.146(2)	130
N2–H2B...O3 <sup>ii</sup>	0.86	2.02	2.829(2)	157
O5–H5A...O1 <sup>iii</sup>	0.78(3)	1.88(3)	2.6528(17)	169(3)
O5–H5B...O3 <sup>i</sup>	0.78(3)	1.89(3)	2.639(2)	161(3)

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x, y - 1/2, -z + 1/2$ ; (iii)  $x - 1, y, z$ ; (iv)  $x + 1, y, z$  for  $C_{30}H_{26}CoN_4O_{10}$ ; (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $x - 1, -y + 1/2, z - 1/2$ ; (iii)  $-x, -y + 1, -z + 1$  for  $C_{30}H_{26}ZnN_4O_{10}$

this mode. Pyridine ring vibration of free nicotinamide at  $1,535\text{ cm}^{-1}$  shifts to  $1,447\text{ cm}^{-1}$  for  $Co^{II}$  complex and  $1,446\text{ cm}^{-1}$  for  $Zn^{II}$  complex in the complexes indicating that the pyridine ring is coordinated. The main difference in the spectrum of coumarilic acid is that the C=O stretching vibration of the carboxyl group at  $1,730\text{ cm}^{-1}$  shifts to lower frequency in the metal complex. The carboxylate bands in the metal complexes appear in the range of  $1,669$  and  $1,670\text{ cm}^{-1}$ , respectively. This shows that the coordination takes place through the carboxyl groups [29].

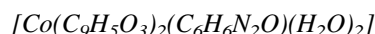
The –OH bending band of coumarilic acid in the metal complex is observed around  $1,472$  and  $1,473\text{ cm}^{-1}$ . The low intensity bands in the region of  $650\text{--}480\text{ cm}^{-1}$  are attributed to M–N and M–O vibrations [27–31].

The frequency of the asymmetric carboxylate vibration,  $\nu_{as}(\text{COO}^-)$ , and the magnitude of the separation between the carboxylate stretches,  $\Delta = \nu_{as}(\text{COO}^-) - \nu_s(\text{COO}^-)$  are often used as spectroscopic criteria to determine the mode of the carboxylate binding. Generally, the following order is proposed for divalent metal carboxylates:

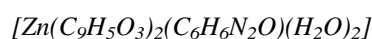
$$\Delta_{(\text{chelating})} < \Delta_{(\text{bridging})} < \Delta_{(\text{ionic})} < \Delta_{(\text{monodentate})}$$

The shift ( $\Delta$ ) between the  $\nu_{\text{sym}}$  and  $\nu_{\text{asym}}$  bands of  $(\text{COO}^-)$  group is  $200$  and  $202\text{ cm}^{-1}$  for complexes, which is more than that for the sodium coumarilate salt ( $143\text{ cm}^{-1}$ ) indicating that monodentate carboxylate group exists [24, 27, 31–33].

### Thermal analysis



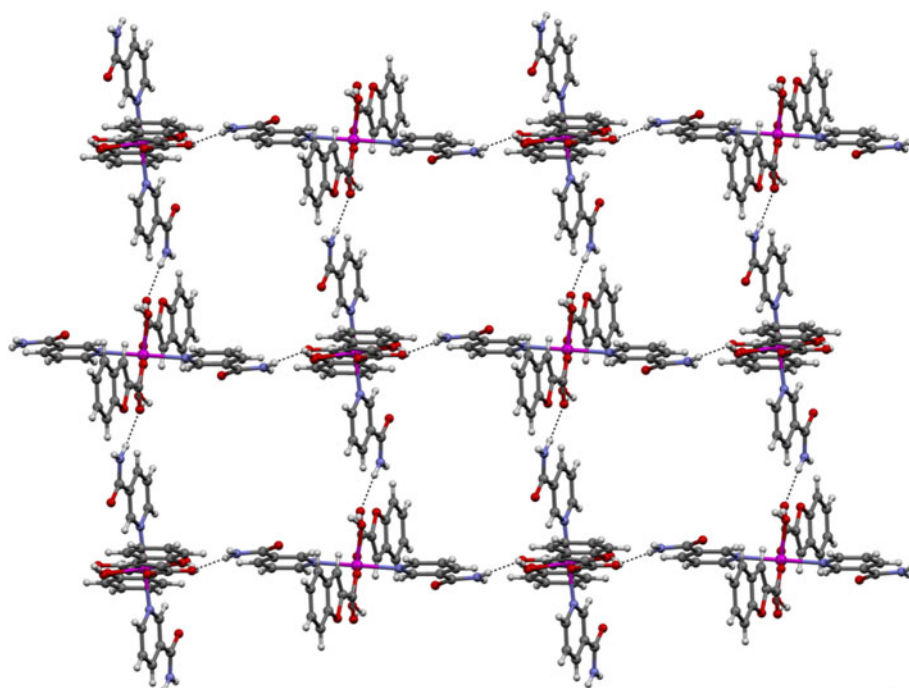
The TG-DTG/DTA curves of  $Co^{II}$  complex were shown in Fig. 1a. The metal complex does not contain any hydrated water. There are 2 mol aqua ligands that remove with two steps. First of them removes in the range of  $123\text{--}158\text{ }^\circ\text{C}$ . The corresponding endothermic DTA peak was appeared at  $148\text{ }^\circ\text{C}$  (exp. 2.72 %; calc. 2.69 %). The other water molecule was evaporated in the range of  $159\text{--}194\text{ }^\circ\text{C}$ . Its endothermic DTA peak is at  $181\text{ }^\circ\text{C}$  (exp. 2.76 %; calc. 2.69 %). Then, in the range of  $195\text{--}26\text{ }^\circ\text{C}$ , one mole nicotinamide ( $C_6H_6N_2O$ ) ligand was lost with an endothermic DTA peak at  $252\text{ }^\circ\text{C}$  (exp. 18.25 %; calc. 18.44). The next decomposition step at the range of  $262\text{--}303\text{ }^\circ\text{C}$  (DTA peak  $272\text{ }^\circ\text{C}$ ) is attributable to loss of 1 mol coumarilate ( $C_9H_5O_3$ ) and amide portion ( $\text{CONH}_2$ ) of nicotinamide ligand. The experimental and calculation data are compatible (exp. 31.07 %; calc. 30.99 %). In the fifth decomposition step, pyridine ( $C_5H_4N$ ) portion of nicotinamide ligand is lost in the range of  $304\text{--}351\text{ }^\circ\text{C}$  with DTA peak at  $341\text{ }^\circ\text{C}$  (exp. 11.51 %; calc. 11.79 %). At the last decomposition step at the range of  $353\text{--}990\text{ }^\circ\text{C}$  was attributed to removing of coumarilate ( $C_9H_5O_3$ ) ligand that is residual organic part of complex (DTA peak  $553\text{ }^\circ\text{C}$ ) (exp. 23.72 %; calc. 24.34 %). The black  $CoO$  residue was obtained in the reaction crucible as decomposition product (exp. 12.59 %; calc. 11.33 %).



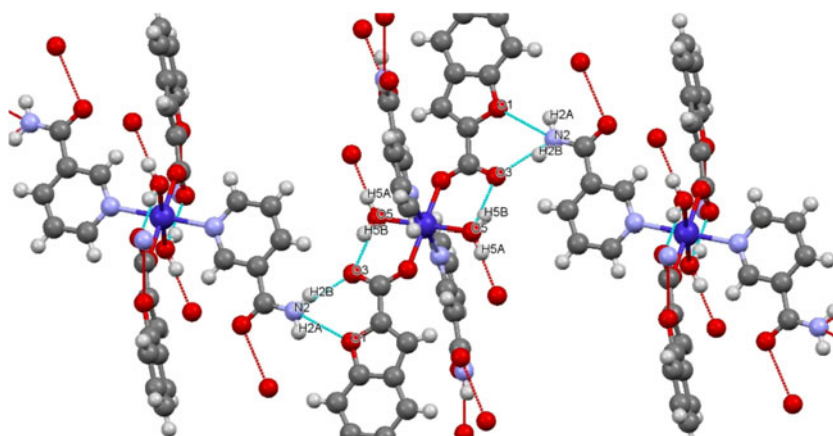
According to TG-DTG/DTA results,  $Zn(II)$ -coumarilate–nicotinamide complex was decomposed in five steps (Fig. 1b). Its decomposition steps are similar to  $Co^{II}$  complex,



**Fig. 4** A view of the crystal structure of **I** and **II**, showing the formation of  $R_4^4(40)$  rings



**Fig. 5** Showing the molecular and intermolecular hydrogen bonds in network lattice (**I** and **II**) structure



but the aqua ligands of  $\text{Zn}^{\text{II}}$  complex were removed in single step (exp. 5.27 %; calc. 5.39 %). Then, 1 mol nicotinamide ligand was leaved from complex at the range of 166–267 °C (DTA max. 243 °C endothermic) (exp. 18.69 %; calc. 18.26 %). In the next three steps, coumarilate, nicotinamide and coumarilate ligands were decomposed and released from complex structure in the same order. The experimental and calculated results were found to be comparable each other. In the reaction crucible, ZnO were found as last decomposition residue (exp. 12.98 %; calc. 12.18 %). The residue of ZnO is black, because it was covered with carbonized carbon.

The thermal decomposition steps, removed products and decomposition temperature range are summarized at Table 2.

#### Mass analysis

The thermal decomposition pathway of the  $[\text{Co}(\text{CCA})_2(\text{NA})_2(\text{H}_2\text{O})_2]$  complex was recorded using direct insertion probe pyrolysis mass spectrometry method (Fig. 2). The mass spectrum shows the fragmentation pattern and the most fragile points of the molecule. The molecular ion peak was not detected in the mass spectrum recorded. A schematic representation including the main fragmentation process for complex and ligands were given in Scheme 2. Beside the most abundant peaks, much fewer abundant peaks observed on the spectrum depend probably on the nature of ligands.



## X-ray diffraction analysis

Suitable crystals of  $\text{C}_{30}\text{H}_{26}\text{CoN}_4\text{O}_{10}$  (**I**) and  $\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_{10}\text{Zn}$  (**II**) were selected for data collection which was performed on a STOE IPDS II diffractometer equipped with a graphite-monochromatic Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 296 K. The structures were solved by direct methods using SHELXS-97 [34] and refined by full-matrix least-squares methods on  $F^2$  using SHELXL-97 [34]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods [35]. Water H atoms were located in a difference map and refined subject to a DFIX restraint of  $\text{O-H} = 0.83(2) \text{ \AA}$ . Other H atoms were located from different maps and then treated as riding atoms with C-H distances of 0.93 and N-H distances of 0.86  $\text{\AA}$ . The following procedures were implemented in our analysis: programme used for molecular graphics were as follow: MERCURY programmes [36]; supramolecular analyses: PLATON [37]; software used to prepare material for publication: WinGX [38]. Other details of cell data, data collection and refinement are summarized in Table 3.

The crystallographic analyses exhibit that the complexes **I** and **II** are isostructural. Complexes  $\text{C}_{30}\text{H}_{26}\text{CoN}_4\text{O}_{10}$  and  $\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_{10}\text{Zn}$  crystallizes in the space group  $P2_1/c$ . The molecular structures of **I** and **II** with the atom numbering schemes are shown in Fig. 3. The asymmetric units of **I** and **II** contain one  $M(\text{II})$  ion [ $M(\text{II}) = \text{Co}(\text{II})$  in **I** and  $\text{Zn}(\text{II})$  in **II**], one nicotinamide ligand, one 2-benzofurancarboxylate ligand and one aqua ligand (Fig. 3).

Each  $M(\text{II})$  [ $M(\text{II}) = \text{Co}(\text{II})$  in **I** and  $\text{Zn}(\text{II})$  in **II**] ion located on a centre of symmetry and is coordinated by two nitrogen atoms [ $\text{N1}$  and  $\text{N1}^i$ ] of nicotinamide ligands, two oxygen atoms [ $\text{O2}$  and  $\text{O2}^i$ ] from 2-benzofurancarboxylate ligands and two oxygen atoms [ $\text{O5}$  and  $\text{O5}^i$ ] from aqua ligands [ $(i) -x + 1, -y + 1, -z + 1$ ]. The coordination geometry around the  $M(\text{II})$  ion [ $M(\text{II}) = \text{Co}(\text{II})$  in **I** and  $\text{Zn}(\text{II})$  in **II**] can be described as a distorted octahedral geometry. The equatorial  $\text{Co-O}$  bond lengths of **I** are 2.0589(10) and 2.0739(10)  $\text{\AA}$  and the axial  $\text{Co-N}$  bond distance is 2.1086(11)  $\text{\AA}$ , respectively. The equatorial  $\text{Zn-O}$  bond lengths of **II** are 2.0947(12) and 2.1151(12)  $\text{\AA}$  and the axial  $\text{Zn-N}$  bond length is 2.1701(13)  $\text{\AA}$ , respectively. The  $\text{O-M-O}$  bond angles are 88.09(4)° and 91.91(4)° in **I** and 88.84(5)° and 91.16(5)° in **II**, respectively. The bond angles of  $\text{N-M-O}$  ranged between 88.20(5)–91.80(5)° in **I** and 88.43(5)–91.57(5)° in **II**, respectively. Selected bond distances and angles for complexes **I** and **II** were given in Table 4.

Molecules of **I** and **II** are linked into sheets by a combination of  $\text{N-H}\cdots\text{O}$  and  $\text{O-H}\cdots\text{O}$  hydrogen bonds (Table 5). In the complexes of **I** and **II**, amino N2 atom in the molecule at  $(x, y, z)$  acts as hydrogen-bond donor, via atom H2B, to atom O3 in the molecule at  $(-x, y - 1/2,$

$-z + 1/2$  for **I** and  $x - 1, -y + 1/2, z - 1/2$  for **II**), so forming a C(10) chain running parallel to the [010] direction. The combination of C(10) chains generates a chain of edge-fused  $R_4^4(40)$  rings running parallel to the  $ab$  plane (Fig. 4). In the complexes of **I** and **II**, amino N2 atom in the molecule at  $(x, y, z)$  acts as hydrogen-bond donor, via atom H2A, to atom O5 in the molecule at  $(x - 1, y, z)$  for **I** and  $-x, -y + 1, -z + 1$  for **II**), so forming a C(8) chain running parallel to the [100] direction. Similarly, water O5 atoms in the molecule at  $(x, y, z)$  acts as hydrogen-bond donors, via atoms H5A, to atoms  $\text{O4}^{\text{iv}}$  in **I** and  $\text{O1}^{\text{iii}}$  in **II**, so forming a C(8) chains running parallel to the [100] direction. The combination of C(8) chains generates a chain of edge-fused  $R_2^2(6)$  rings running parallel to the [100] direction. Each complex, there are also two  $\pi\cdots\pi$  interactions between pyridine and benzene rings. The  $\pi\cdots\pi$  interactions play a major role in constructing network.

The stability of complex structure is provided by intramolecular strong hydrogen bonds formed between hydrogens molecules and carbonyl oxygen of ligand water (Fig. 5).

## Conclusions

The structure of complexes contain one  $M^{\text{II}}$  ion [ $M^{\text{II}} = \text{Co}(\text{II})$  and  $\text{Zn}(\text{II})$ ], two nicotinamide ligand, two 2-benzofurancarboxylate ligand and two aqua ligand. Each metal cation located on a centre of symmetry and is coordinated by two nitrogen atoms of nicotinamide ligands, two oxygen atoms from 2-benzofurancarboxylate ligands and two oxygen atoms from aqua ligands. The coordination geometry around the metal ions can be described as a distorted octahedral geometry. Network lattice structure is formed through hydrogen bonding between carbonyl oxygen and ketonic oxygen of coumarilic acid and amide hydrogens of nicotinamide. The thermal decomposition of the title complex takes place in three steps: dehydration, elimination of nicotinamide ligands and decomposition of coumarilate ligands. This decomposition manner is similar to those previously reported for some mixed nicotinamide-carboxylate metal complexes [28–33, 35]. Early releasing of the nicotinamide before the salicylate ligand by volatilisation may be due to non-ionic bonding of this ligand with  $\text{Zn}(\text{II})$  ion.

## Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center: CCDC-933362 for  $\text{C}_{30}\text{H}_{26}\text{CoN}_4\text{O}_{10}$  and 933360 for  $\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_{10}\text{Zn}$  contain the supplementary

crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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