# Synthesis, physico-chemical characterization and thermal behavior of new complexes with $N_4O_2$ donor set

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Abstract Three new coordinative compounds of the type  $[Co(en)_2CO_3]\cdot 0.75H_2O$  (1) and  $[M(en)_2(H_2O)_2]CO_3$  ((2) M:Ni, (3) M:Cu; en: ethylenediamine) were synthesized and characterized. The IR and UV–Vis spectral data indicate that ethylenediamine acts as chelate, while carbonate ions act as bidentate chelate ligand for (1)/counter ion for (2) and (3) generating complexes with octahedral stereo-chemistry. The thermal behavior provided confirmation of the complexes composition, as well as the number and the nature of water molecules and the intervals of thermal stability. The biological assays revealed a good activity against *Enterococcus faecium* for copper complex.

**Keywords** Ethylenediamine · Carbonate · Complex · Thermal behavior

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#### Introduction

Ethylenediamine (en) is an organic compound with many applications. In coordination chemistry, it functions usually as chelate ligand [1–3], seldom bridging ligand [4] or is involved in condensation reactions with different compounds affording new ligands [5, 6]. An unusual behavior of ethylenediamine has been reported [7] when it occurred a Michael reaction with acrylic acid in the presence of Ni(II) ions, leading to a new ligand, ethylenediamino-N,N-dipropionate dianion and to its' corresponding complex.

Ethylenediamine complexes are widely investigated due to their interesting structures and to their importance in various areas. For example, three varieties of H-bonding interactions have been evidenced in the case of  $[Ni(H_2-O)_2(en)_2](4-nba)_2$  (nba = 4-nitrobenzoate) that led to interesting supramolecular interactions [1].

There are studies that describe the investigation of effects of nickel ethylenediamine complexes on preparation of some catalysts [8]. Also, copper ethylenediamine complexes exhibit catalytic activity in autooxidation of phenols [9]. Cobalt complexes of type  $[Co(en)_2L]^{3+}$  (L = bipyridine, 1,10-phenanthroline, pyrazole) possess high antibacterial and antifungal activity [10]. Investigation of antitumor properties of platinum compound  $[Pt(en)(pyridine)Cl]NO_3$  indicated significant cytotoxic activity against HL-60 [11].

Even if coordination compounds that contain complex ion  $[Ni(en)_2(H_2O)_2]^{2+}$  are reported in literature for a long time [1, 12, 13], there is lack of information regarding carbonate ion as counter ion.

As interest in ethylenediamine complexes is continuously growing, we report herein the synthesis, thermal decomposition, and biologic activity of three new ethylenediamine complexes:  $[Co(en)_2CO_3] \cdot 0.75H_2O$  (1),

**Table 1** Crystallographic data, details of data collection and structure refinement parameters for compound  $[Ni(en)_2(H_2O)_2]CO_3$ 

| Chemical formula                          | $C_5H_{20}N_4NiO_5$                        |  |
|---|--|--|
| $M/g \text{ mol}^{-1}$                    | 274.93                                     |  |
| Temperature/K                             | 298  |  |
| Wavelength/Å                              | 0.71073                                    |  |
| Crystal system                            | orthorombic                                |  |
| Space group                               | Ccmb(64)                                   |  |
| a/Å                                       | 7.0796(6)                                  |  |
| <i>b</i> /Å                               | 24.549(2)                                  |  |
| c/Å                                       | 10.6986(12)                                |  |
| Cell volume/Å <sup>3</sup>                | 1859.39(30)                                |  |
| Cell ratio                                | a/b = 0.2884; b/c = 2.2946<br>c/a = 1.5112 |  |
| Ζ   | 4  |  |
| Calculated density/g cm <sup>-3</sup>     | 1.16773                                    |  |
| Goodness-of-fit on $F^2$                  | 1.035                                      |  |
| Final <i>R1</i> , $wR_2 [I > 2\sigma(I)]$ | 0.0667; 0.1963                             |  |
| <i>R</i> 1, $wR_2$ (all data)             | 0.0725; 0.2047                             |  |

 $[Ni(en)_2(H_2O)_2]CO_3$  (2),  $[Cu(en)_2(H_2O)_2]CO_3$  (3). For nickel complex (2) is presented X-ray structure also.

#### Experimental

#### Materials and methods

All chemicals were purchased from Sigma-Aldrich, reagent grade and were used without further purification.

Chemical analysis has been performed using a EuroEA elemental analyser (for C, N and H) and a Shimadzu AA 6300 spectrometer (for metallic ion). IR spectra were recorded in KBr pellets with a Bruker Tensor 37 spectrometer in the range  $400-4,000 \text{ cm}^{-1}$ .

Electronic spectra by diffuse reflectance technique, with Spectralon as standard, were recorded in the range 200–1,500 nm, on a Jasco V 670 spectrophotometer.

The heating curves (TG and DTA) were recorded using a Labsys 1200 SETARAM instrument, with a sample mass of 6–12 mg over the temperature range of 30–900 °C, using a heating rate of 5 °C min<sup>-1</sup>. The measurements were carried out in synthetic air (flow rate 16.66 mL<sup>3</sup> min<sup>-1</sup>) using alumina crucibles.

The X-ray powder diffraction patterns were collected on a DRON-3 diffractometer with a nickel filtered Cu  $K_{\alpha}$ radiation ( $\lambda = 1.5418$  Å) in 2 $\theta$  range of 5–70°, a step width of 0.05° and an acquisition time of 2 s per step.

X-ray data for crystal  $[Ni(en)_2(H_2O)_2]CO_3$  were collected at room temperature on a STOE IPDS II

diffractometer. The structure was solved by direct methods and refined by full-matrix least squares techniques based on  $F^2$ . The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97 crystallographic software package. A summary of the crystallographic data and the structure refinement for crystal [Ni(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]CO<sub>3</sub> is given in Table 1. The detailed structural data have been deposited with CCDC-989475.

In vitro antimicrobial tests were carried out by an adapted agar-disk diffusion technique using 0.5 McFarland suspension of bacteria obtained from 24 h cultures. The antimicrobial activities of the newly synthesized compounds were determined against American Type Culture Collection (ATCC) reference and clinical microbial strains, *i.e.*, Gram negative (*Escherichia coli* ATCC 25922), Gram positive (*Staphylococcus aureus* ATCC 6538, *Bacillus subtilis* 6683, *Enterococcus faecium* E5), and fungal strains (*Candida albicans* 1760).

The compounds were dissolved in water to a final concentration of 1 mg mL<sup>-1</sup>. A volume of 10  $\mu$ L of each tested compounds solution was distributed directly on the solid medium previously seeded with the microbial inoculums. The inoculated plates were incubated for 24 h at 37 °C. Antimicrobial activity was assessed by measuring the growth inhibition zones diameters [14–16].

The quantitative assay of the minimal inhibitory concentration (MIC,  $\mu g \ mL^{-1}$ ) was based on liquid medium twofold microdilutions. After 24 h incubation at 37 °C, the bactericidal activity was quantified by measuring the absorbance of the liquid culture at 620 nm. At the end of the experiment, the wells were emptied, washed three times with PBS, fixed with cold methanol and stained with 1 % violet crystal solution for 30 min. The biofilm formed on plastic wells was resuspended in 30 % acetic acid. The intensity of the colored suspensions was assessed by measuring the absorbance at 490 nm [14–16].

#### Synthesis of complexes

All the complexes were obtained following the general procedure: a mixture formed from metal carbonate (Co) or basic carbonate (Ni, Cu), ethylenediamine (in the molar ratio 1 M:1en) and 25 mL distilled water was stirred at room temperature for 8 h. The obtained suspension was filtered off, and the solution was left at room temperature for several days. The sparingly soluble obtained products were filtered off, washed several times with ethanol and air-dried.

The compounds are soluble in water, alcohols, dimethylformamide, and dimethylsulfoxide.

[Co(en)<sub>2</sub>CO<sub>3</sub>]·0.75H<sub>2</sub>O (**1**). *Analysis found*: Co, 23.28; C, 23.25; H, 7.04; N, 22.30 %; *requires for* 

Synthesis, physico-chemical characterization and thermal behavior

**Table 2** Selected absorption maxima for complexes/cm<sup>-1</sup>

|         |         | 1       |   |
|---------|---------|---------|---|
| (1)     | (2)     | (3)     | Assignments                               |
| 3,421 m | 3,400 m | 3,440 m | $\nu(H_2O)$                               |
| 3,332 s | 3,371 s | 3,368 s | $v_{as}(NH_2)$                            |
| 3,296 s | 3,227 s | 3,310 s |   |
| 3,245 m | 3,181 m | 3,220 m | $\nu_s(NH_2)$                             |
| 3,171 m | 3,120 m | 3,138 m |   |
| 2,945 m | 2,970 m | 2,963 w | $v_{as}(CH_2)$                            |
| 2,883 m | 2,905 m | 2,883 w | $v_s(CH_2)$                               |
| 1,586 m | 1,589 m | 1,586 m | $\delta(NH_2)$                            |
| 1,546 m | -       | -       | $v_1(CO_3)$ chelate                       |
| -       | 1,463 m | 1,456 s | $v_3(CO_3)$ free ion                      |
| 1,276 m | -       | -       | $v_5(CO_3)$ chelate                       |
| 1,030 s | -       | -       | v <sub>2</sub> (CO <sub>3</sub> ) chelate |
| -       | 836 m   | 851 m   | $v_2(CO_3)$ free ion                      |
| -       | 690 m   | 697 m   | $v_4(CO_3)$ free ion                      |
| 657 m   | -       | -       | $v_6(CO_3)$ chelate                       |
| -       | 646 w   | 524 m   | $\rho_{\rm w}({\rm H_2O})$                |

 $CoC_5H_{17.5}N_4O_{3.75}$ : Co, 23.32; C, 23.77; H, 6.98; N, 22.47 %. Reaction yield 90 %

 $[Ni(en)_2(H_2O)_2]CO_3 (2) \ Analysis \ found: \ Ni, \ 21.27; \ C, \\ 22.03; \ H, \ 7.26; \ N, \ 20.41 \ \%; \ requires \ for \ NiC_5H_{20}N_4O_5; \ Ni, \\ 21. \ 35; \ C, \ 21.84; \ H, \ 7.33; \ N, \ 20.52 \ \%. \ Reaction \ yield \ 75 \ \%.$ 

 $\label{eq:cuency} \begin{array}{l} [Cu(en)_2(H_2O)_2]CO_3 \ \textbf{(3)} \ \textit{Analysis found:} \ Cu, \ 22.80; \ C, \\ 21.39; \ H, \ 7.31; \ N, \ 19.97 \ \%; \ \textit{requires for} \ CuC_5H_{20}N_4O_5; \ Cu, \\ 22.71; \ C, \ 21.46; \ H, \ 7.20; \ N, \ 20.02 \ \%. \ Reaction \ yield \ 85 \ \%. \end{array}$ 

#### **Results and discussion**

The reaction of metal carbonates (M: Co, Ni, Cu) with ethylenediamine in the molar ratio 1 M:1en yields complexes of the general type  $M(en)_2CO_3 \cdot nH_2O$ . The compounds were fully characterized by elemental analysis, IR, electronic spectra, thermal analysis and, for nickel complex, single crystal X-ray diffraction. The elemental analysis allows the formulation of complexes as follows:

 $CoC_5H_{17.5}N_4O_{3.75}$  or  $[Co(en)_2CO_3] \cdot 0.75H_2O$  (1) NiC<sub>5</sub>H<sub>20</sub>N<sub>4</sub>O<sub>5</sub> or  $[Ni(en)_2(H_2O)_2]CO_3$  (2) CuC<sub>5</sub>H<sub>20</sub>N<sub>4</sub>O<sub>5</sub> or  $[Cu(en)_2(H_2O)_2]CO_3$  (3)

#### Infrared spectra

Infrared spectra of the metal complexes provide useful information about the nature of the ligands [17]. The main absorption bands of the compounds are listed in Table 2.

The IR spectra of all complexes contain, in the  $2,880-3,370 \text{ cm}^{-1}$  range, absorption bands due to the stretching vibrations of the primary amine and methylene group confirming the presence of ethylenediamine ligand.



Fig. 1 IR spectra of complexes (1) and (3)

The most important bands in the IR spectra are those assigned to carbonate ion, which are different depending of its nature (ligand or counter ion). Thus, the free carbonate ion, of higher symmetry (D<sub>3h</sub>), presents three IR active vibrations  $(v_2 \div v_4)$  and one Raman active  $(v_1)$ . These are preserved even for a lower symmetry  $(D_3)$  as expect for complexes with carbonate ion in the ionization sphere. Since the IR spectra of complexes (2) and (3) contain only these bands, we assumed the presence of carbonate ion as counter ion (Fig. 1). When carbonate ion is coordinated (uni- or bidentate), its symmetry decreases. As a consequence, the  $v_1$  vibration becomes IR active and the two doubly degenerate vibrations ( $v_3$  and  $v_4$ ) splits into two bands. Accordingly, the IR spectra of this kind of complexes contain up to six bands. Furthermore, the splitting of the degenerate vibrations is larger in the bidentate than in unidentate coordination. Based on these literature data [17], we assumed a chelate coordination of carbonate ion for complex (1).

A broad band in the 3,400–3,440 cm<sup>-1</sup> range that appears in all spectra can be assigned to v(OH) stretching vibration of water molecules, presence confirmed by elemental and thermal analyses as well. Additional bands at 646 and 525 cm<sup>-1</sup> for complexes (2) and (3), respectively, assigned to  $\rho_w(H_2O)$  vibration mode, indicate that the water molecules are involved in coordination as well [17].

#### Electronic spectra

The features of electronic spectra of complexes offer information concerning the oxidation state of the metallic ion, stereochemistry, as well as the ligand field strength. Table 3 lists the electronic absorption bands, their assignments as well the crystal field parameters (10Dq, B and  $\beta$ ) calculated with König formulas [18].

| Compound | Absorption maxima/cm <sup>-1</sup> | Assignments   | Crystal field parameters |             |      |
|----------|------------------------------------|---|--------------------------|-------------|------|
|          |                                    |   | 10Dq/cm <sup>-1</sup>    | $B/cm^{-1}$ | β    |
| (1)      | 38,460                             | $\pi \to \pi^*$   | 12,700                   | 711         | 0.73 |
|          | 19,600                             | ${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}(P)$                  |                          |             |      |
|          | 11,760                             | ${}^{4}T_{1g} \rightarrow {}^{4}A_{2g}$                     |                          |             |      |
|          | 6,900                              | ${}^{4}T_{1g} \rightarrow {}^{4}T_{2g}$                     |                          |             |      |
| (2)      | 46,500                             | $\pi \rightarrow \pi^*$                                     | 11,050                   | 898         | 0.86 |
|          | 28,600                             | ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$                  |                          |             |      |
|          | 18,020                             | ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$                     |                          |             |      |
|          | 14,490                             | ${}^{3}A_{2g} \rightarrow {}^{1}E_{g}$                      |                          |             |      |
|          | 11,050                             | ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$                     |                          |             |      |
| (3)      | 37,040                             | $\pi \rightarrow \pi^*$                                     |                          |             |      |
|          | 31,250                             | LMCT  |                          |             |      |
|          | 14,085                             | $d_{\mathrm{z}^2}  ightarrow d_{\mathrm{x}^2-\mathrm{y}^2}$ |                          |             |      |
|          | 17,090                             | $d_{\rm xy,yz, \ xz} \rightarrow d_{\rm x^2-y^2}$           |                          |             |      |

Table 3 Absorption maxima from electronic spectra of complexes (1)-(3), assignments and crystal field parameters

LMCT ligand to metal charge transfer

An intense band in the UV region of the complexes spectra was assigned to  $\pi \rightarrow \pi^*$  transition arising from the C=O moiety of carbonate.

Three additional bands appear in the electronic spectrum of the Co(II) complex assigned to spin allowed transitions for an octahedral geometry. The broad aspect of the bands arises from lower symmetry generated by different nature of ligands and donor atoms, respectively [19]. The splitting parameter value of 12,700 cm<sup>-1</sup> is close to an average value for a [Co(II)N<sub>4</sub>O<sub>2</sub>] chromophore, while the nephel-auxetic parameter of 0.73 is an indicative of a higher degree of covalency.

The Ni(II) complex (2) exhibits an octahedral geometry as indicate the three bands that can be assigned to spin allowed transitions [19]. The low intensity band at  $14,490 \text{ cm}^{-1}$  is assigned to the spin forbidden transition  ${}^{3}A_{2g} \rightarrow {}^{1}E_{g}$ . The splitting parameter value of 11,050 cm<sup>-1</sup> is in accordance with an [Ni(II)N<sub>4</sub>O<sub>2</sub>] chromophore having a high number of donor atoms that generate a strong field, such nitrogen ones, while the nephelauxetic parameter of 0.86 is an indicative of a lower degree of covalency (Table 3).

The electronic spectrum of the Cu(II) complex exhibits a characteristic broad band with a maximum at 14,085 cm<sup>-1</sup> tentatively assigned to  $d_{z^2} \rightarrow d_{x^2-y^2}$  transition and a shoulder at higher energy, pattern characteristic for a distorted octahedral stereochemistry [19]. The charge transfer band is observed at 31,250 cm<sup>-1</sup> only for complex (3) having in view that Cu(II) is more easily to reduce in comparison with both Co(II) and Ni(II).



Fig. 2 Perspective view of the complex  $[Ni(en)_2(H_2O)_2]CO_3$  with the atom labeling scheme

Description of crystal structure

A perspective view of the complex (2) along with the atom labels is shown in Fig. 2. Selected bond distances and angles are given in Table 4.

The crystallographic investigation reveals a mononuclear unit that contain complex ion  $[Ni(en)_2(H_2O)_2]^{2+}$  and  $CO_3^{2-}$ ion as counter ion. The coordination geometry of the nickel ion is octahedral. Four nitrogen atoms that arise from two ethylenediamine molecules form the basal plane of coordination polyhedra. Ethylenediamine acts as bidentate chelate ligand, coordination manner that is often encountered for this ligand [1–3]. The lengths of all Ni–N bonds have the same value [2.091(**3**) Å] and are slightly shorter than Ni–O bonds that are also equal [2.174(**3**) Å]. Two coordinated water molecules occupy the apical positions. The Ni(II) ion and both oxygen atoms that belongs to water molecules are collinear, this suggesting a quite regular octahedral coordination. According to packing diagrams (Figs. 3, 4), carbonate ion is disordered on two crystalographic positions with 0.5 occupancies each.

For the complexes (1) and (3), on the basis of all physico-chemical data the proposed coordination is presented Fig. 5.

Thermal behavior of complexes

The results regarding the thermal decomposition of complexes in synthetic air, using a heating rate of 5 grd min<sup>-1</sup>, are presented in the following section and all data are summarized in the Table 5.

| Distances/Å           |          | Angles/°                                |            |
|-----------------------|----------|---|------------|
| N1-Ni1                | 2.091(3) | N1 <sup>ii</sup> –Ni1–N1 <sup>iii</sup> | 83.65(16)  |
| Ni1-N1 <sup>ii</sup>  | 2.091(3) | N1 <sup>ii</sup> –Ni1–N1                | 96.35(16)  |
| Ni1-N1 <sup>iii</sup> | 2.091(3) | N1 <sup>iii</sup> –Ni1–N1               | 180.00(11) |
| Ni1-N1 <sup>i</sup>   | 2.091(3) | N1 <sup>ii</sup> –Ni1–N1 <sup>i</sup>   | 180.00(11) |
| Ni1-O1 <sup>ii</sup>  | 2.174(3) | N1 <sup>iii</sup> -Ni1-N1 <sup>i</sup>  | 96.35(16)  |
| Ni1-O1                | 2.174(3) | N1-Ni1-N1 <sup>i</sup>                  | 83.65(16)  |
|                       |          | N1 <sup>ii</sup> –Ni1–O1 <sup>ii</sup>  | 91.39(10)  |
|                       |          | N1 <sup>iii</sup> –Ni1–O1 <sup>ii</sup> | 88.61(10)  |
|                       |          | N1-Ni1-O1 <sup>ii</sup>                 | 91.39(10)  |
|                       |          | N1 <sup>i</sup> –Ni1–O1 <sup>ii</sup>   | 88.61(10)  |
|                       |          | N1 <sup>ii</sup> –Ni1–O1                | 88.61(10)  |
|                       |          | N1 <sup>iii</sup> -Ni1-O1               | 91.39(10)  |
|                       |          | N1-Ni1-O1                               | 88.61(10)  |
|                       |          | N1 <sup>i</sup> -Ni1-O1                 | 91.39(10)  |
|                       |          | O1 <sup>ii</sup> –Ni1–O1                | 180.00(0)  |

Symmetry code: (i) -x, y, 1 - z; (ii) x, 1 - y, z; (iii) -x, 1 - y, 1 - z; (iv) -1 - x, y, 1 - z

**Fig. 3** Packing diagram of complex [Ni(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]CO<sub>3</sub> along [111] direction



According to TG, DTG, and DTA curves (Fig. 6) the first decomposition step which occurs in the temperature range 77–110 °C, corresponds to the loss of water molecules. The anhydrous compound is stable over 70 °C temperature range. The second thermal event can be associated with the release of ethylenediamine molecules. Taking into account of thermal effects (an endothermic one followed by an exothermic one), we could assume that at the beginning only Co–N bonds cleavage occurs, the process being an endothermic one. Once the temperature increases,



Fig. 4 Packing diagram of complex  $[Ni(en)_2(H_2O)_2]CO_3$  along [112] direction



ethylenediamine molecules suffer oxidative degradation (the exothermic effect). The IR spectrum recorded for the intermediate isolated at the maximum in DTG curve (275 °C) exhibits only CoCO<sub>3</sub> vibration bands.

Finally, the third stage of decomposition is associated with decomposition of  $CoCO_3$  to cobalt mixt oxide  $Co_3O_4$  as powder XRD analyses of the final residues indicate (ASTM 78-1970).

Thermal decomposition of complex  $[Ni(en)_2(H_2O)_2]CO_3$ 

Decomposition of complex (2) starts at 90 °C with one of water molecules loss (Fig. 7).

The second thermal event is a complex one, being an overlap of at least three processes as both DTA and DTG curves indicates. It comprises the second water molecule and ethylenediamine molecules elimination. The remaining nickel carbonate decomposes to nickel oxocarbonate (NiCO<sub>3</sub>·2NiO) and finally to NiO.



Fig. 5 The proposed formulation for complexes (1) and (3)



Fig. 6 TG, DTG and DTA curves for [Co(en)<sub>2</sub>CO<sub>3</sub>]·0.75H<sub>2</sub>O (1)



Fig. 7 TG, DTG and DTA curves for [Ni(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]CO<sub>3</sub> (2)

 Table 5
 Thermal degradation data (in synthetic air) for the complexes

| Complex  | Step | Thermal effect | Temperature range/°C | $\Delta m_{exp} / \%$ | $\Delta m_{calc} / \%$ |
|--|------|----------------|----------------------|-----------------------|------------------------|
| $[Co(en)_2CO_3] \cdot 0.75H_2O(1)$   | 1    | Endothermic    | 77–110               | 5.2                   | 5.3                    |
|  | 2    | Miscellaneous  | 180–275              | 47.7                  | 47.6                   |
|  | 3    | Exothermic     | 275–345              | 15.2                  | 15.3                   |
| Residue (Co <sub>3</sub> O <sub>4</sub> )  |      |                |                      | 31.9                  | 31.8                   |
| [Ni(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]CO <sub>3</sub> ( <b>2</b> ) | 1    | Endothermic    | 90–145               | 7.0                   | 6.6                    |
|  | 2    | Exothermic     | 160–375              | 49.7                  | 50.2                   |
|  | 3    | Exothermic     | 375-465              | 10.9                  | 10.7                   |
|  | 4    | Exothermic     | 465–520              | 5.4                   | 5.3                    |
| Residue (NiO)  |      |                |                      | 27.0                  | 27.2                   |
| [Cu(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]CO <sub>3</sub> ( <b>3</b> ) | 1    | Endothermic    | 75–135               | 13.1                  | 12.9                   |
|  | 2    | Exothermic     | 135–210              | 42.8                  | 43.0                   |
|  | 3    | Exothermic     | 210–390              | 5.0                   | 5.2                    |
|  | 4    | Exothermic     | 390–470              | 10.6                  | 10.5                   |
| Residue (CuO)  |      |                |                      | 28.5                  | 28.4                   |



Fig. 8 TG, DTG, and DTA curves for  $[Cu(en)_2(H_2O)_2]CO_3$  (3)

## Thermal decomposition of complex [Cu(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]CO<sub>3</sub>

Unlike compound (2), the complex (3) loses both water molecules in the first stage of decomposition (Fig. 8) as both DTG and DTA curves show. The remaining product is not stable, undergoing the ethylenediamine loss. The obtained copper carbonate slowly (210–390 °C) decomposes in copper oxocarbonate (2CuCO<sub>3</sub>·CuO). After 390 °C, the strong exothermic stage is associated with its decomposition to CuO.

#### **Biological** activity

The antibacterial activity was determined in vitro against using American Type Culture Collection (ATCC) reference and clinical bacterial strains, *i.e.*, Gram negative (*Escherichia coli* ATCC 25922), Gram positive (*Staphylococcus aureus* ATCC 6538, *Bacillus subtilis* 6683, *Enterococcus faecium* E5), and fungal strains (*Candida albicans* 1760).

A literature survey revealed that ethylenediamine complexes reported in literature possess high antibacterial and antifungal activity [10]. In our case, from all tested complexes only complex (**3**) exhibited a good activity against *Enterococcus faecium* E5, with a MIC value of  $125 \ \mu g \ mL^{-1}$ ; for the other tested strains, the inhibitory activity was lower or has been missing at the tested concentrations range.

### Conclusions

Three new ethylenediamine complexes of the type  $[Co(en)_2CO_3] \cdot 0.75H_2O$  (1) and  $[M(en)_2(H_2O)_2]CO_3$  ((2) M:Ni, (3) M:Cu; en: ethylenediamine) have been

synthesized and characterized. Spectral data revealed the chelate coordination of ethylenediamine, meanwhile carbonate acts as bidentate chelate for complex (1) and counter ion for (2) and (3).

The structural features of complex (2) were fully revealed by single crystal X-ray analysis.

In the case of all complexes, metallic ions are encountered in an octahedral environment, quite distorted in the case of complex (3).

The thermal decomposition have confirmed the complexes formula and provided information concerning the presence of crystallization or coordination water molecules.

Taking into account their similar composition, complexes (2) and (3) decompose respecting a similar pattern. The final products in all cases were the most stable metal oxides.

The screening of antibacterial activity revealed that only complex (3) exhibits good activity against *Enterococcus faecium* E5, with a MIC value of 125  $\mu$ g mL<sup>-1</sup>.

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