

## Synthesis, Spectroscopic Studies, Molecular Modeling and Antimicrobial Activity of Binuclear Ni(II) Complexes of 4,6-Diacetylresorcinol

Magdy Shebl\*, Saied M.E. Khalil, A. Taha and M.A.N. Mahdi

Department of Chemistry, Faculty of Education, Ain Shams University, Roxy, Cairo 11341, Egypt  
[magdy\\_shebl@hotmail.com](mailto:magdy_shebl@hotmail.com)

**Abstract:** Reactions of 4,6-diacetylresorcinol with different Ni(II) salts *viz.*, OAc<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, in both presence and absence of LiOH, yielded a new series of binuclear Ni(II) complexes that reflect the non-coordinating or weakly coordinating power of the ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> anions as compared to the strongly coordinating power of OAc<sup>-</sup> and Cl<sup>-</sup> anions. Reactions of the ligand with nickel(II) ion in the presence of a secondary ligand (L') [O,O-donor; acetylacetone (acac), N,O-donor; 8-hydroxyquinoline (8-HQ) or, N,N-donor; 1,10-phenanthroline (Phen) and 2,2'-bipyridyl (Bpy)] in 1:2:2 (L:M:L') molar ratio yielded mixed-ligand complexes with two molar ratios 2:2:2 (L:M:L') (complexes **6**, **7** and **8**) and 1:2:1 (L:M:L') (complexes **9** and **10**). The metal complexes were characterized by elemental and thermal analyses, IR, electronic and mass spectra as well as conductivity and magnetic susceptibility measurements. The analytical and spectroscopic data suggested that the H<sub>2</sub>L ligand acts as a neutral, monobasic or dibasic tetradentate ligand, depending on the pH of the medium, through the two phenolic and two carbonyl groups. Electronic spectra, magnetic and conductivity measurements showed that all complexes are octahedral with non-electrolytic nature except complex **3** that has a 1:2 electrolytic nature. Molecular orbital calculations were performed for the ligands and their complexes using *Hyperchem 7.52* program on the bases of PM3 level and the results were correlated with the experimental data. The free ligand and its nickel(II) complexes showed antimicrobial activity towards some of Gram-positive and Gram-negative bacteria, yeast (*Candida albicans*) and fungus (*Aspergillus fumigatus*).

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### 1. Introduction

The bioinorganic chemistry of nickel [1–3] has been rapidly expanded due to the increasing number of nickel complexes of biological interest reported in the literature. In this context structurally characterized nickel complexes have been able to act as antiepileptic [4], anticonvulsant [5] agents or vitamins [6] or have shown antibacterial, antifungal [7–12] and anticancer/antiproliferative [13–16] activity.

Mixed-ligand complexes have been extensively studied following recognition that they play an important role in biological processes and serve as suitable models for valuable information in the elucidation of enzymatic processes of biological relevance [17,18]. Also, these complexes showed significant antifungal, antibacterial and anticancer activity [19,20].

4,6-diacetylresorcinol (H<sub>2</sub>L) contains the chemically active carbonyl and phenolic OH groups. Therefore it has been used for generation of different flexible polydentate ligands [21–27]. Consequently, there has been a considerable interest in the coordination chemistry of 4,6-diacetylresorcinol. However, literature survey revealed that few papers [28–30] reporting the synthesis and characterization of mixed-ligand complexes including 4,6-diacetylresorcinol as a primary ligand.

As a part of our continuing study of metal complexes of 4,6-diacetylresorcinol, we report here the preparation, spectroscopic characterization and biological activity of some binuclear nickel(II) complexes, together with the molecular orbital modeling to understand and explain the structural parameters of the current compounds in molecular terms.

### 2. Experimental

#### 2.1. Materials

4,6-Diacetylresorcinol was prepared as cited in the literature [31]. Metal salts, lithium hydroxide, acetylacetone, 8-hydroxyquinoline, 1,10-phenanthroline, 2,2'-bipyridyl, EDTA disodium salt, ammonium hydroxide, murexide and nitric acid were either Aldrich, BDH or Merck products. Organic solvents (ethanol, diethylether, dimethylformamide (DMF) and dimethylsulfoxide (DMSO)) were reagent grade chemicals and were used without further purification.

#### 2.2. Synthesis of the metal complexes

An ethanolic solution of the metal salt (30 mL) was added gradually to the ethanolic solution of the ligand (40 mL) in the molar ratio 2:1 (M:L). The reaction mixture was heated under reflux for 7 h. The resulting precipitate was filtered off, washed with ethanol then diethylether and finally air-dried. The

following detailed preparations are given as examples and the other complexes were obtained similarly.

### 2.2.1. Synthesis of the [(H<sub>2</sub>L)Ni<sub>2</sub>(OAc)<sub>4</sub>]·EtOH, complex (1)

Nickel(II) acetate tetrahydrate, Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (1.285 g, 5.16 mmol) in ethanol (30 mL) was added gradually with constant stirring to the solution of the ligand, H<sub>2</sub>L, (0.5 g, 2.58 mmol) in ethanol (30 mL). The reaction mixture was heated under reflux for 7 h. A pale pink precipitate was formed, filtered off and washed several times with small amounts of ethanol then diethylether and finally air-dried. The yield was 0.5 g (33 %), m.p. >300 °C.

### 2.2.2. Synthesis of the [(L)Ni<sub>2</sub>(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·H<sub>2</sub>O·0.5EtOH, complex (2)

Lithium hydroxide monohydrate, LiOH·H<sub>2</sub>O (0.217 g, 5.17 mmol) in the least amount of bidistilled water (10 mL) was added gradually with constant stirring to the solution of the ligand, H<sub>2</sub>L, (0.5 g, 2.58 mmol) in ethanol (30 mL), in molar ratio 2:1 (LiOH:H<sub>2</sub>L). Nickel(II) acetate tetrahydrate, Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (1.285 g, 5.16 mmol) in ethanol (30 mL) was added gradually with constant stirring to the above mixture. The resulting mixture was heated under reflux for 7 h. A beige precipitate was formed, filtered off and washed several times with small amounts of bidistilled water, ethanol then diethylether and finally air-dried. The yield was 0.75 g (54%), m.p. >300 °C.

### 2.2.3. Synthesis of the [(HL)<sub>2</sub>Ni<sub>2</sub>(acac)<sub>2</sub>]·7.5H<sub>2</sub>O, complex (6)

Lithium hydroxide monohydrate, LiOH·H<sub>2</sub>O (0.217 g, 5.17 mmol) in the least amount of bidistilled water (10 mL) was added gradually with constant stirring to the solution of the ligand, H<sub>2</sub>L, (0.5 g, 2.58 mmol) in ethanol (30 mL), in molar ratio 2:1. Nickel(II) acetate tetrahydrate, Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (1.285 g, 5.16 mmol) in ethanol (30 mL) was added gradually with constant stirring to the above mixture then a solution of acetylacetone, (acac) (0.517 gm, 5.16 mmol) in ethanol was added. The resulting mixture was heated under reflux for 7 h. A pale green precipitate was formed, filtered off and washed several times with small amounts of bidistilled water, ethanol then diethylether and finally air-dried. The yield was 0.45 g (42%), m.p. >300 °C.

### 2.2.4. Unsuccessful trials

Several trials to isolate Ni(II) complexes, in absence of LiOH, by using NiSO<sub>4</sub>, Ni(NO<sub>3</sub>)<sub>2</sub> or Ni(ClO<sub>4</sub>)<sub>2</sub> were unsuccessful. These trials gave oily products which were not isolated in pure forms.

## 2.3. Analytical and physical measurements

Elemental analyses were performed at the Microanalytical Center, Cairo University, Giza, Egypt. Analysis of nickel(II) ion followed dissolution of the solid complexes in hot concentrated nitric acid then diluting with bidistilled water and filtration. The solution was neutralized with ammonia solution and

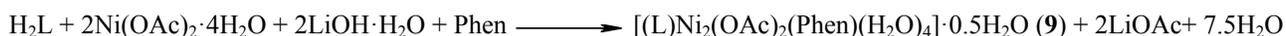
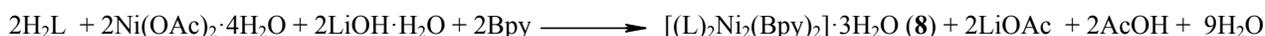
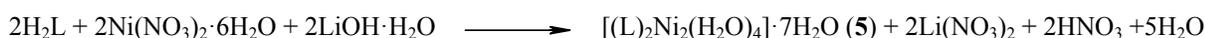
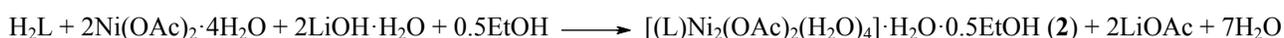
the metal ion was then titrated with EDTA following standard literature method [32]. Melting points of the ligand and its metal complexes were determined using a Stuart melting point instrument. Infrared spectra were recorded in the region (4000–400 cm<sup>-1</sup>) using KBr discs on a Shimadzu 4000 IR spectrophotometer. Electronic spectra were recorded at room temperature on a Jasco model V-550 UV/Vis spectrophotometer as Nujol mulls and/or solutions in DMF. The magnetic susceptibility measurements were carried out at room temperature using a magnetic susceptibility balance of the type Johnson Matthey, Alfa product, Model No. (MKI). Effective magnetic moments were calculated from the expression  $\mu_{eff.} = 2.828 (\chi_M \cdot T)^{1/2}$  B.M., where  $\chi_M$  is the molar susceptibility corrected using Pascal's constants for the diamagnetism of all atoms in the compounds [33]. Molar conductivities of 10<sup>-3</sup> M solutions of the solid complexes in DMF were measured on the Corning conductivity meter NY 14831 model 441. Mass spectra were recorded at 290 °C and 70 eV on a Hewlett-Packard mass spectrometer model MS-5988. The thermogravimetric analyses of the solid complexes were carried out from room temperature to 800 °C using a Shimadzu-50 thermal analyzer. The biological activity of the ligand and its metal complexes was studied using the disc diffusion method [34]

## 2.4. Antimicrobial Activity

The standardized disc-agar diffusion method [34] was followed to determine the activity of the synthesized compounds. The investigated bacteria were seeded in test tubes with nutrient broth (NB) 10<sup>8</sup> cells/ml, and homogenized in agar suspensions then poured into Petri dishes. The holes (diameter 4 mm) were done in the cool medium, after incubation for 16 h in a thermostat at 30 °C, the inhibition (sterile) zone diameters (including disc) were measured and expressed in mm. The tested compounds were dissolved in dimethylformamide (DMF) solvent and prepared in two concentrations; 100 and 50 mg/mL and then 10 µL of each preparation was dropped using a micropipette on disc-agar of 6 mm in diameter and the concentrations became 1 and 0.5 mg/disk respectively. An inhibition zone diameter over 6 mm indicates that the tested compound is active against the sensitive organisms used: *Staphylococcus aureus* (ATCC 25923) and *Bacillus subtilis* (ATCC 6635) as Gram-positive bacteria, *Escherichia coli* (ATCC 25922) and *Salmonella typhimurium* (ATCC 14028) as Gram-negative bacteria, yeast; *Candida albicans* (ATCC 10231) and fungus; *Aspergillus fumigatus*. Three replicates were carried out for each extract against each of the test organism. The antibiotic chloramphenicol was used as standard reference in the case of Gram-negative bacteria, cephalothin for Gram-positive bacteria and cycloheximide for yeasts and fungi.

## 3. Results and discussion

Reactions of the ligand, H<sub>2</sub>L with various Ni(II) salts *viz.*, OAc<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, in presence and absence of LiOH, were studied. In case of acetate and chloride salts, the ligand acts as a neutral tetradentate ligand in absence of LiOH (complexes **1** and **3**) while it acts as a dibasic tetradentate ligand in presence of LiOH (complexes **2** and **4**). On the other hand, reactions with nitrate, sulphate or perchlorate salts were only successful in the presence of LiOH, yielding the same complex (complex **5**) regardless the anion used. The obtained complexes reflect the non-coordinating or weakly coordinating power of the ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> anions as compared to the strongly coordinating power of OAc<sup>-</sup> and Cl<sup>-</sup> anions. Also, the ligand was allowed to react with nickel(II) ion in the presence of a secondary ligand (L') [O,O-donor; acetylacetone (acac), N,O-donor; 8-hydroxyquinoline (8-HQ) or, N,N-donor; 1,10-H<sub>2</sub>L + 2Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O + EtOH → [(H<sub>2</sub>L)Ni<sub>2</sub>(OAc)<sub>4</sub>]·EtOH (**1**) + 8H<sub>2</sub>O



### 3.1. IR spectra

The significant IR spectral data of the ligand and its nickel(II) complexes and their tentative assignments are listed in Table 2. The IR spectra of the current complexes showed a broad band in the region 3181-3503 cm<sup>-1</sup>, which can be assigned to the stretching vibrations, ν(O-H), of the hydroxyl group in water or ethanol molecules and/or the coordinated phenolic groups. Also, the strong band at 1660 cm<sup>-1</sup> assigned to ν(C=O) of the ligand was shifted to lower wave numbers (1595-1650 cm<sup>-1</sup>) in all complexes. This indicates the participation of the carbonyl oxygen in chelation [35,36]. To ascertain the involvement of the phenolic group in coordination, this requests to make a follow up of the stretching vibration bands of ν(C-O) in all complexes. This check shows that the ν(C-O) was shifted from 1047 cm<sup>-1</sup> in case of H<sub>2</sub>L free ligand to (1049-1069) cm<sup>-1</sup> in the complexes in addition to decrease of their intensities, pointing to the involvement of the phenolic oxygen in the coordination [21,23]. Complexes **1** and **2** showed new bands located at 1535 and 1469 cm<sup>-1</sup> for the former complex and at 1536 and 1467 cm<sup>-1</sup> for the latter one. These two bands may due to ν<sub>as</sub>(COO<sup>-</sup>) and ν<sub>s</sub>(COO<sup>-</sup>), respectively of the acetate group. The separation of the two bands in the complexes **1** and **2**, Δν = (ν<sub>as</sub>-ν<sub>s</sub>) = 66 and 69 cm<sup>-1</sup>, respectively, is comparable to the values cited for the bidentate character of the acetate group [21,37,38]; Δν = 75-80 cm<sup>-1</sup>. On the other hand, complex **9** showed

phenanthroline (Phen) and 2,2'-bipyridyl (Bpy)] in 1:2:2 (L:M:L') molar ratio yielding mixed-ligand complexes with two molar ratios 2:2:2 (L:M:L') (complexes **6**, **7** and **8**) and 1:2:1 (L:M L') (complexes **9** and **10**). The prepared complexes are found to be stable at room temperature, non-hygroscopic and insoluble in water and most common organic solvents. The melting points of the complexes are found to be above 300 °C. The metal complexes were characterized by elemental and thermal analyses, IR, electronic and mass spectra as well as conductivity and magnetic susceptibility measurements. The analytical and physical data of the metal complexes are listed in Table 1. The elemental analyses of the metal complexes agreed well with the proposed formulas.

The following representative equations illustrate the formation of some of the prepared complexes:

ν<sub>as</sub>(COO<sup>-</sup>) and ν<sub>s</sub>(COO<sup>-</sup>) bands at 1500 and 1328 cm<sup>-1</sup>, respectively. The higher difference (135 cm<sup>-1</sup>) between the two bands indicates the monodentate nature of the acetate group [39-41]. The mixed-ligand complexes containing 8-hydroxyquinoline (**7**), 2,2'-bipyridyl (**8**) and 1,10-phenanthroline (**9** and **10**) showed new bands in the range 1502-1535 cm<sup>-1</sup> (Table 2), compared to those reported for ν(C=N) of the free 8-HQ, Bpy and Phen at 1586, 1570 and 1560 cm<sup>-1</sup>, respectively [42,43] supporting the coordination of the C=N group to the metal ion [26,44]. The above interpretation is further supported by the appearance of weak to medium intensity absorption bands which are absent in the free ligand at: 465-594 and 412-446 cm<sup>-1</sup> that may be attributed to ν(M-O) and ν(M-N); respectively [21,23,45,46].

### 3.2. Conductivity measurements

The molar conductance values of the current complexes were measured at room temperature for their DMF solutions (10<sup>-3</sup> M) and the results are listed in Table 3. The values showed that all complexes have non-electrolytic nature except complex **3** which gave molar conductance value = 185.9 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, suggesting its 1:2 electrolytic nature. This suggestion is further supported by precipitation of Cl<sup>-</sup> ions when AgNO<sub>3</sub> solution was added to the DMF solution of the complex. In case of complexes **6** and **7**, the relatively high values of the molar conductance data may be due to the partial dissociation in their DMF solutions,

however, they did not reach the previously reported values for 1:1 electrolytes in DMF solutions (~70-110)  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  [47]. The neutrality of the current complexes may be attributed to either partially/completely de-protonation of the phenolic OH groups of the free ligand during the complexation with the metal ions, and/or coordinating of the acetate or chloride anions of the metal salt. Further support in favour of coordination by the anions comes from the IR data which proves that the H<sub>2</sub>L ligand acts as neutral, monobasic or dibasic tetradentate fashion *via* acetyl and phenolic groups.

### 3.3. Electronic spectra and magnetic moment measurements

Electronic spectra of the nickel(II) complexes (Table 3) were examined as DMF solutions and/or Nujol mulls for sparingly soluble complexes. Comparison of the spectrum of the free ligand with its complexes showed the persistence of the bands for the ligand in all complexes. However, the bands were slightly shifted to blue or red regions of the spectrum in all complexes. Also, new bands were observed in the spectra of the complexes which are listed in Table 3.

Usually, the spectra of octahedral Ni(II) consist of three bands which are accordingly assigned as  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  [48]. In the electronic spectra of the complexes, the first  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$  transition was not observed due to the fact that, it occurs in the near infrared and it is out of the range of the used instrument. The second  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  transition was observed in the region 564-710 nm while the third  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  was observed in the region 484-596 nm. The room-temperature magnetic moments of the binuclear nickel(II) complexes are in the range 2.92-3.3 B.M. which lie in the range (2.9-3.3 B.M.) of the octahedral nickel(II) complexes [49], suggesting the absence of any antiferromagnetic interaction. Thus, based on the electronic spectral and magnetic moment data, nickel(II) complexes have the octahedral geometry with its characteristic features.

### 3.4. Thermal analysis

Thermal gravimetric analysis (TGA) was mainly used to proof the associated water or solvent molecules to be in the coordination sphere or in the outer sphere of the complex [50]. Complexes **2**, **6**, **7** and **10** were taken as representative examples for thermal analysis. The results of thermal analysis of these complexes (Table 4) are in agreement with elemental analyses.

The thermogram of complex (**2**),  $[(L)Ni_2(OAc)_2(H_2O)_4] \cdot H_2O \cdot 0.5EtOH$ , shows three stages of decomposition in the range 36-320 °C. The first one in the range 36–92 °C, is due to the loss of half uncoordinated ethanol molecule as well as uncoordinated water molecule (weight loss; Calc./Found%; 7.58/7.22%). The second stage in the

range 92-171 °C and is due to the loss of two coordinated water molecules (weight loss; Calc./Found%; 6.66/6.20%). The third stage in the range 171-320 °C and is due to the loss of two coordinated water molecules as well as an acetic acid molecule (weight loss; Calc./Found%; 17.30/17.75%). The decomposition pattern of complex **2** has been explained by the reactions shown in Scheme 1.

The thermogram of complex (**10**),  $[(L)Ni_2Cl_2(Phen)(H_2O)_4] \cdot 3.5H_2O$ , (Fig. 1) shows three stages of decomposition in the range 36-380 °C. The first one in the range 36–96 °C, is due to the loss of 3.5 uncoordinated water molecules (weight loss; Calc./Found%; 9.05/8.94%). The second stage in the range 96-180 °C and is due to the loss of two coordinated water molecules (weight loss; Calc./Found%; 5.17/4.90%). The third stage in the range 180-380 °C and is due to the loss of two coordinated water molecules as well as two HCl molecules (weight loss; Calc./Found%; 15.66/15.20%). The decomposition pattern of complex **10** has been explained by the reactions shown in Scheme 2.

### 3.5. Mass spectra

The mass spectral studies of the representative complexes **2**, **6** and **9** have been carried out and their spectra are depicted in Fig. 2. The complexes **2**, **6** and **9** showed the molecular ion peaks at  $m/z$  500, 702 and 680, respectively which compare very well with the calculated formula weights of the non-hydrated or solvated complexes  $[(L)Ni_2(OAc)_2(H_2O)_4]$  (F. Wt = 499.71),  $[(HL)_2Ni_2(acac)_2]$  (F. Wt = 702.12) and  $[(L)Ni_2(OAc)_2(Phen)(H_2O)_4]$  (F. Wt = 679.96). The fragmentation patterns of the complexes showed a fragment with  $m/z$  194 due to the H<sub>2</sub>L ligand, supporting their structures.

Finally, from the interpretation of elemental and thermal analyses and spectral data (infrared, electronic and mass) as well as conductivity and magnetic susceptibility measurements at room temperature, it is possible to draw up the tentative structures of the metal complexes. Figs. 3-5 represent the proposed structures of the metal complexes.

### 3.6. Molecular modeling

The major thrust of quantum chemical research is to understand and explain the structural parameters of the current compounds in molecular terms. In order to support experimental data obtained from various measurements *viz.*, spectral methods, quantum chemical calculations were conducted and also to provide molecular-level understanding of the observed experimental behaviour. All quantum chemical properties were obtained after geometrical optimization using semiempirical at *PM3* level provided by the *hyperchem 7.52* program. Fig. 6 represents the optimized structure of complex **5** as a representative complex. Various computed quantum chemical indices such as the energies of the lowest unoccupied ( $E_{LUMO}$ )

and highest occupied molecular orbitals ( $E_{\text{HOMO}}$ ) and  $\Delta E_{\text{gap}}$  ( $\Delta E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ ) and dipole moment ( $\mu$ ) of the ligands and their complexes are listed in Table 5. Frontier orbital theory is useful in predicting the extent of interaction between ligands and metal ion. Terms involving the frontier molecular orbital (FMO) could provide dominative contribution, because of the inverse dependence of stabilization energy on orbital energy difference [51]. Moreover, the gap between the HOMO and LUMO energy levels of the molecules was another important factor that should be considered. In the literature, it is well established that the higher the HOMO energy ( $E_{\text{HOMO}}$ ) of the ligand, the greater the trend of offering electrons to vacant d orbitals of the metal ion, and the higher the efficiency of interaction between ligands and nickel(II); in addition, the lower the LUMO energy of the free ligands, the easier the HOMO acceptance of electrons from metal ion, as the LUMO–HOMO energy gap decreased, interactions between the reacting species become stronger and as a result the stability of the formed Ni(II)-complexes.

The structural parameters of the ligands and their complexes, given in Table 5, are correlated with the current experimental data (Table 2) as shown in Fig. 7:  $\Delta E_{\text{gap}} = 8.11 - 0.043 \Delta \nu_{\text{C=O}}(\text{Lig-comp})$ ,  $r = 0.95$  ( $n = 7$ , except complexes **5-7, 10**). The negative slope of this linear plot indicates increasing of the  $\Delta \nu_{\text{C=O}}(\text{Lig-comp})$  bond strength with the decrease of  $\Delta E_{\text{gap}}$  i.e., as the bond interaction between the carbonyl of free  $\text{H}_2\text{L}$  ligand and metal ion increases. Thus the stronger M-O bond (decreasing  $\Delta E_{\text{gap}}$  values). This finding is emphasized by the positive slope of the linear relationship between  $E_{\text{HOMO}}$  and  $\Delta \nu_{\text{C=O}}$ :  $E_{\text{HOMO}} = -9.374 + 0.034 \Delta \nu_{\text{C=O}}(\text{Lig-comp})$ ,  $r = 0.89$  ( $n = 7$ , except complexes **1,2,5,10**) shown as insert in Fig. 7. This conclusion is in accord with the results obtained for related copper(II) and nickel(II) chelates [52, 53].

The linear correlation of the stretching frequency of  $\Delta \nu_{\text{C=O}}(\text{Lig-comp})$  with the calculated dipole moment ( $\mu/\text{D}$ ) of the prepared complexes (Table 5);  $\mu/\text{D} = 14.19 - 0.139 \Delta \nu_{\text{C=O}}(\text{Lig-comp})$ ,  $r = 0.93$  ( $n = 7$ , except complexes **4,7,8,10**). The negative slope recommends increasing of the dipole moment with the decreasing of the ligand field stabilization energy.

### 3.7. Antimicrobial studies

In order to test whether the synthesized complexes are active against microorganisms, they were tested against the sensitive organisms *Staphylococcus aureus* (ATCC 25923) and *Bacillus subtilis* (ATCC 6635) as Gram-positive bacteria, *Escherichia coli* (ATCC 25922) and *Salmonella typhimurium* (ATCC 14028) as Gram-negative bacteria, yeast: *Candida albicans* (ATCC 10231) and fungus: *Aspergillus fumigatus*. The results are listed in Table 6. The data showed that the  $\text{H}_2\text{L}$  ligand and its nickel(II) complexes exhibit a little activity against

these organisms. The element, nickel, plays an ambivalent role in biological systems. While it is fundamental to numerous microbial enzymes, it is also very toxic if supplied in higher concentration. The present antimicrobial testing results are consistent with the previous findings that chelation of the nickel(II) ion with ligands increases their biological activities. A possible explanation for the observed increased activity upon chelation is that the positive charge of the metal in chelated complex is partially shared with the ligand's donor atoms so that there is an electron delocalization over the whole chelate ring. This, in turn, will increase the lipophilic character of the metal [54,55].

Complex **10**,  $[(\text{L})\text{Ni}_2\text{Cl}_2(\text{Phen})(\text{H}_2\text{O})_4] \cdot 3.5\text{H}_2\text{O}$ , showed the highest activity towards the Gram-positive bacteria (*Staphylococcus aureus*) while complex **7**,  $[(\text{HL})_2\text{Ni}_2(8\text{-HQ})_2] \cdot 2\text{H}_2\text{O} \cdot \text{EtOH}$  showed the highest activity towards Gram-positive bacteria (*Bacillus subtilis*). Also, the same complex (**7**) seems to be promising since it showed the highest activity towards the Gram-negative bacteria (*Salmonella typhimurium*). Against *Escherichia coli* and *Candida albicans*, complexes **2**,  $[(\text{L})\text{Ni}_2(\text{OAc})_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O} \cdot 0.5\text{EtOH}$ , and **5**,  $[(\text{L})_2\text{Ni}_2(\text{H}_2\text{O})_4] \cdot 7\text{H}_2\text{O}$ , showed the highest activity. Finally, against *Aspergillus fumigatus*, the ligand and only two complexes **3** and **5** that showed a lower activity.

### 4. Conclusion

A new series of Ni(II) complexes have been synthesized by reactions of several Ni(II) salts with 4,6-diacetylresorcinol, in presence and absence of LiOH. Reactions in the presence of a secondary ligand (L') [O,O-donor; acetylacetone, N,O-donor; 8-hydroxyquinoline or N,N-donor; 1,10-phenanthroline or 2,2'-bipyridyl] yielded mixed-ligand complexes. The metal complexes were characterized by elemental and thermal analyses, IR, electronic and mass spectra as well as conductivity and magnetic susceptibility measurements. The obtained complexes are octahedral binuclear complexes with molar ratios; 1:2 and 2:2 (L:M) and mixed-ligand complexes with 2:2:2 and 1:2:1 (L:M:L') molar ratios. The spectroscopic data showed that the ligand acts as a neutral, monobasic or dibasic tetradentate ligand through the two carbonyl oxygen atoms and the two oxygen atoms of the two phenolic groups. Molecular orbital calculations were performed for the ligands and their complexes and the results were correlated with the experimental data. The ligand and some of its metal complexes showed antimicrobial activity towards selected kinds of Gram-positive bacteria, Gram-negative bacteria, yeast and fungus.

Table 1 Analytical and physical data of the metal complexes of H<sub>2</sub>L ligand

No.	Reaction	Complex M. F. [F. Wt]	Color	Yield (%)	Elemental analysis, % found/(calc.)				
					C	H	N	Cl	M
(1)	H <sub>2</sub> L + Ni(OAc) <sub>2</sub>	[(H <sub>2</sub> L)Ni <sub>2</sub> (OAc) <sub>4</sub> ].EtOH (C <sub>20</sub> H <sub>28</sub> O <sub>13</sub> Ni <sub>2</sub> ) [593.86]	Pale pink	33	40.86 (40.45)	4.54 (4.75)	---	---	19.30 (19.77)
(2)	H <sub>2</sub> L + Ni(OAc) <sub>2</sub> + LiOH	[(L)Ni <sub>2</sub> (OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].H <sub>2</sub> O.0.5EtOH (C <sub>15</sub> H <sub>27</sub> O <sub>13.5</sub> Ni <sub>2</sub> ) [540.79]	Beige	54	33.09 (33.32)	4.94 (5.03)	---	---	21.30 (21.71)
(3)	H <sub>2</sub> L + NiCl <sub>2</sub>	[(H <sub>2</sub> L) <sub>2</sub> Ni <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>2</sub> .4H <sub>2</sub> O (C <sub>20</sub> H <sub>32</sub> O <sub>14</sub> Cl <sub>4</sub> Ni <sub>2</sub> ) [755.70]	Pale pink	77	31.53 (31.79)	4.70 (4.27)	---	18.30 (18.77)	15.90 (15.54)
(4)	H <sub>2</sub> L + NiCl <sub>2</sub> + LiOH	[(L)Ni <sub>2</sub> Cl <sub>2</sub> (EtOH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].2EtOH (C <sub>18</sub> H <sub>40</sub> O <sub>12</sub> Cl <sub>2</sub> Ni <sub>2</sub> ) [636.84]	Pale pink	39	33.64 (33.95)	6.00 (6.33)	---	10.80 (11.13)	18.20 (18.44)
(5)	H <sub>2</sub> L + Ni(NO <sub>3</sub> ) <sub>2</sub> + LiOH	[(L) <sub>2</sub> Ni <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].6H <sub>2</sub> O* (C <sub>20</sub> H <sub>36</sub> O <sub>18</sub> Ni <sub>2</sub> ) [681.92]	Beige	61	34.91 (35.23)	5.60 (5.32)	---	---	16.90 (17.22)
(6)	H <sub>2</sub> L + Ni(OAc) <sub>2</sub> + LiOH + acac	[(HL) <sub>2</sub> Ni <sub>2</sub> (acac) <sub>2</sub> ].7.5H <sub>2</sub> O (C <sub>30</sub> H <sub>47</sub> O <sub>19.5</sub> Ni <sub>2</sub> ) [837.12]	Pale green	42	43.25 (43.04)	5.72 (5.66)	---	---	13.80 (14.03)
(7)	H <sub>2</sub> L + Ni(OAc) <sub>2</sub> + LiOH + 8- HQ	[(HL) <sub>2</sub> Ni <sub>2</sub> (8-HQ) <sub>2</sub> ].2H <sub>2</sub> O.EtOH** (C <sub>40</sub> H <sub>40</sub> N <sub>2</sub> O <sub>13</sub> Ni <sub>2</sub> ) [874.19]	Green	69	54.70 (54.96)	5.00 (4.61)	3.50 (3.20)	---	13.70 (13.43)
(8)	H <sub>2</sub> L + Ni(OAc) <sub>2</sub> + LiOH + Bpy	[(L) <sub>2</sub> Ni <sub>2</sub> (Bpy) <sub>2</sub> ].3H <sub>2</sub> O (C <sub>40</sub> H <sub>38</sub> N <sub>4</sub> O <sub>11</sub> Ni <sub>2</sub> ) [868.19]	Green	67	55.44 (55.34)	4.80 (4.41)	6.41 (6.45)	---	13.98 (13.52)
(9)	H <sub>2</sub> L + Ni(OAc) <sub>2</sub> + LiOH + Phen	[(L)Ni <sub>2</sub> (OAc) <sub>2</sub> (Phen)(H <sub>2</sub> O) <sub>4</sub> ].0.5H <sub>2</sub> O (C <sub>26</sub> H <sub>31</sub> N <sub>2</sub> O <sub>12.5</sub> Ni <sub>2</sub> ) [688.96]	Green	52	45.10 (45.33)	4.20 (4.54)	4.00 (4.07)	---	17.40 (17.04)
(10)	H <sub>2</sub> L + NiCl <sub>2</sub> + LiOH + Phen	[(L)Ni <sub>2</sub> Cl <sub>2</sub> (Phen)(H <sub>2</sub> O) <sub>4</sub> ].3.5H <sub>2</sub> O (C <sub>22</sub> H <sub>31</sub> N <sub>2</sub> O <sub>11.5</sub> Cl <sub>2</sub> Ni <sub>2</sub> ) [695.82]	Beige	43	37.70 (37.98)	4.20 (4.49)	3.70 (4.03)	9.70 (10.19)	16.40 (16.88)

\* The same complex was obtained by using NiSO<sub>4</sub> or Ni(ClO<sub>4</sub>)<sub>2</sub>.\*\* The same complex was obtained by using NiCl<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, NiSO<sub>4</sub> or Ni(ClO<sub>4</sub>)<sub>2</sub>.Table 2 Characteristic IR spectral data of the ligand H<sub>2</sub>L and its metal complexes

No.	complex	IR spectra (cm) <sup>-1</sup>				
		v(OH) H <sub>2</sub> O / EtOH/ phenolic	v(C=O) )	v(C=C) )	v(C-O)	Other bands
1	H <sub>2</sub> L [(H <sub>2</sub> L)Ni <sub>2</sub> (OAc) <sub>4</sub> ].EtOH	3430 3384	1660 1650	1588 1605	1047 1052	1535; v <sub>as</sub> (COO <sup>-</sup> ), 1469 v <sub>s</sub> (COO <sup>-</sup> ); (bidentate OAc <sup>-</sup> )
2	[(L)Ni <sub>2</sub> (OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].H <sub>2</sub> O.0.5Et OH	3385	1645	1601	1052	1536; v <sub>as</sub> (COO <sup>-</sup> ), 1467 v <sub>s</sub> (COO <sup>-</sup> ); (bidentate OAc <sup>-</sup> )
3	[(H <sub>2</sub> L) <sub>2</sub> Ni <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>2</sub> .4H <sub>2</sub> O	3320	1623	1581	1069	
4	[(L)Ni <sub>2</sub> Cl <sub>2</sub> (EtOH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].2EtOH	3385	1625	1540	1052	
5	[(L) <sub>2</sub> Ni <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].6H <sub>2</sub> O	3372	1646	1601	1052	
6	[(HL) <sub>2</sub> Ni <sub>2</sub> (acac) <sub>2</sub> ].7.5H <sub>2</sub> O	3419	1647	1609	1069	
7	[(HL) <sub>2</sub> Ni <sub>2</sub> (8-HQ) <sub>2</sub> ].2H <sub>2</sub> O.EtOH	3181	1605	1578	1069	1502; v(C=N) (8-HQ)
8	[(L) <sub>2</sub> Ni <sub>2</sub> (Bpy) <sub>2</sub> ].3H <sub>2</sub> O	3503	1598	1567	1053	1520; v(C=N) (Bpy)
9	[(L)Ni <sub>2</sub> (OAc) <sub>2</sub> (Phen)(H <sub>2</sub> O) <sub>4</sub> ].0.5H 2O	3385	1595	1570	1049	1500 v <sub>as</sub> (COO <sup>-</sup> ), 1328 v <sub>s</sub> (COO <sup>-</sup> ) (monodentate OAc <sup>-</sup> ), 1516; v(C=N)(Phen)
10	[(L)Ni <sub>2</sub> Cl <sub>2</sub> (Phen)(H <sub>2</sub> O) <sub>4</sub> ].3.5H <sub>2</sub> O	3362	1645	1601	1051	1535; v(C=N)(Phen)

Table 3 Electronic spectra, magnetic moments and molar conductivity data of the H<sub>2</sub>L ligand and its metal complexes

No.	Complex	Electronic spectral bands <sup>a</sup> (nm)	$\mu_{\text{eff.}}$ <sup>c</sup> B.M.	$\mu_{\text{compl.}}$ <sup>d</sup> B.M.	Conductance <sup>a</sup> ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )
	H <sub>2</sub> L	300,370	-	-	-
1	[(H <sub>2</sub> L)Ni <sub>2</sub> (OAc) <sub>4</sub> ].EtOH	514,565 (512,570) <sup>b</sup>	2.92	4.04	15.2
2	[(L)Ni <sub>2</sub> (OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].H <sub>2</sub> O.0.5EtOH	(510,564) <sup>b</sup>	3.28	4.72	18.9
3	[(H <sub>2</sub> L) <sub>2</sub> Ni <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>2</sub> .4H <sub>2</sub> O	(510,710) <sup>b</sup>	3.15	4.40	185.9
4	[(L)Ni <sub>2</sub> Cl <sub>2</sub> (EtOH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].2EtOH	(512,567) <sup>b</sup>	3.19	4.82	18.45
5	[(L) <sub>2</sub> Ni <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].6H <sub>2</sub> O	(510,569) <sup>b</sup>	3.21	4.50	5.6
6	[(HL) <sub>2</sub> Ni <sub>2</sub> (acac) <sub>2</sub> ].7.5H <sub>2</sub> O	510,654 (508) <sup>b</sup>	3.11	4.27	36.9
7	[(HL) <sub>2</sub> Ni <sub>2</sub> (8-HQ) <sub>2</sub> ].2H <sub>2</sub> O.EtOH	(484,652) <sup>b</sup>	3.29	4.74	46.6
8	[(L) <sub>2</sub> Ni <sub>2</sub> (Bpy) <sub>2</sub> ].3H <sub>2</sub> O	685 (583) <sup>b</sup>	3.30	5.61	3.82
9	[(L)Ni <sub>2</sub> (OAc) <sub>2</sub> (Phen)(H <sub>2</sub> O) <sub>4</sub> ].0.5H <sub>2</sub> O	685 (596) <sup>b</sup>	3.10	4.28	15.9
10	[(L)Ni <sub>2</sub> Cl <sub>2</sub> (Phen)(H <sub>2</sub> O) <sub>4</sub> ].3.5H <sub>2</sub> O	(512,565) <sup>b</sup>	3.27	4.61	15.5

<sup>a</sup> Solutions in DMF (10<sup>-3</sup> M).<sup>b</sup> Nujol mull.<sup>c</sup>  $\mu_{\text{eff.}}$  is the magnetic moment of one cationic species in the complex.<sup>d</sup>  $\mu_{\text{compl.}}$  is the total magnetic moments of all cations in the complex.Table 4 Thermal analyses data (TG) of some metal complexes of the H<sub>2</sub>L ligand

Complex	Temperature range (°C)	% Wt. loss found/(calc.)	Lost fragment (No. of molecules)
[(L)Ni <sub>2</sub> (OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].H <sub>2</sub> O.0.5EtOH ( <b>2</b> )	36-92	7.22/(7.58)	1 H <sub>2</sub> O (hyd.) + 0.5 EtOH (solv.)
	92-171	6.20/(6.66)	2 H <sub>2</sub> O (coord.)
	171-320	17.30/(17.75)	2 H <sub>2</sub> O (coord.) + 1 acetic acid
[(HL) <sub>2</sub> Ni <sub>2</sub> (acac) <sub>2</sub> ].7.5H <sub>2</sub> O ( <b>6</b> )	24-140	15.86/(16.13)	7.5 H <sub>2</sub> O (hyd.)
[(HL) <sub>2</sub> Ni <sub>2</sub> (8-HQ) <sub>2</sub> ].2H <sub>2</sub> O.EtOH ( <b>7</b> )	35-222	9.20/(9.38)	2 H <sub>2</sub> O (hyd.) + 1 EtOH (solv.)
[(L)Ni <sub>2</sub> Cl <sub>2</sub> (Phen)(H <sub>2</sub> O) <sub>4</sub> ].3.5H <sub>2</sub> O ( <b>10</b> )	36-96	8.94/(9.05)	3.5 H <sub>2</sub> O (hyd.)
	96-180	4.90/(5.17)	2 H <sub>2</sub> O (coord.)
	180-380	15.20/(15.66)	2 H <sub>2</sub> O (coord.) + 2 HCl

Table 5 Structural parameters of the current ligands and their metal complexes.

No.	Complex	Heat of formation	Dipol moment	Energy HOMO	Energy LUMO	$\Delta E_{\text{gap}}$
	H <sub>2</sub> L	-149.74	2.166	-9.480	-0.756	8.724
	Acac	-82.69	3.087	-10.914	-0.440	10.475
	8-HQ	4.80	2.073	-8.804	-0.587	8.217
	Bpy	62.39	0.003	-9.329	-0.710	8.619
	Phen	71.30	2.995	-9.149	-0.843	8.306
1	[(H <sub>2</sub> L)Ni <sub>2</sub> (OAc) <sub>4</sub> ].EtOH	-968.13	4.764	-7.710	-0.501	7.209
2	[(L)Ni <sub>2</sub> (OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].H <sub>2</sub> O.0.5EtOH	-1063.96	4.695	-7.590	-0.406	7.184
3	[(H <sub>2</sub> L) <sub>2</sub> Ni <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].Cl <sub>2</sub> .4H <sub>2</sub> O	-840.01	8.568	-7.743	-1.462	6.281
4	[(L)Ni <sub>2</sub> Cl <sub>2</sub> (EtOH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].2EtOH	-954.71	13.26	-7.958	-1.143	6.815
5	[(L) <sub>2</sub> Ni <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].6H <sub>2</sub> O	-935.27	5.053	-6.517	0.427	6.09
6	[(HL) <sub>2</sub> Ni <sub>2</sub> (acac) <sub>2</sub> ].7.5H <sub>2</sub> O	-943.42	4.397	-8.188	-0.382	7.806
7	[(HL) <sub>2</sub> Ni <sub>2</sub> (8-HQ) <sub>2</sub> ].2H <sub>2</sub> O.EtOH	-765.31	4.756	-7.966	-0.798	7.168
8	[(L) <sub>2</sub> Ni <sub>2</sub> (Bpy) <sub>2</sub> ].3H <sub>2</sub> O	-550.27	3.557	-6.780	-1.410	5.37
9	[(L)Ni <sub>2</sub> (OAc) <sub>2</sub> (Phen)(H <sub>2</sub> O) <sub>4</sub> ].0.5H <sub>2</sub> O	-977.16	10.82	-7.175	-1.657	5.518
10	[(L)Ni <sub>2</sub> Cl <sub>2</sub> (Phen)(H <sub>2</sub> O) <sub>4</sub> ].3.5H <sub>2</sub> O	-796.06	15.49	-7.096	-1.942	5.154

Table 6 Antimicrobial activity of the ligand and some of its metal complexes

Organism	Mean* of zone diameter, nearest whole mm.											
	Gram - positive bacteria				Gram - negative bacteria				Yeasts and Fungi**			
	<i>Staphylococcus aureus</i> (ATCC 25923)		<i>Bacillus subtilis</i> (ATCC 6635)		<i>Salmonella typhimurium</i> (ATCC 14028)		<i>Escherichia coli</i> (ATCC 25922)		<i>Candida albicans</i> (ATCC 10231)		<i>Aspergillus fumigatus</i>	
Concentration	1 mg/ml	0.5 mg/ml	1 mg/ml	0.5 mg/ml	1 mg/ml	0.5 mg/ml	1 mg/ml	0.5 mg/ml	1 mg/ml	0.5 mg/ml	1 mg/ml	0.5 mg/ml
Sample												
H <sub>2</sub> L	3 L	-	3 L	-	2 L	-	3 L	-	3 L	-	2 L	-
[(H <sub>2</sub> L)Ni <sub>2</sub> (OAc) <sub>4</sub> ].EtOH (1)	6 L	3 L	3 L	-	3 L	-	5 L	2 L	5 L	2 L	-	-
[(L)Ni <sub>2</sub> (OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].H <sub>2</sub> O.0.5EtOH (2)	6 L	3 L	9 L	5 L	6 L	4 L	6 L	3 L	5 L	3 L	-	-
[(H <sub>2</sub> L) <sub>2</sub> Ni <sub>2</sub> Cl <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> .4H <sub>2</sub> O (3)	3 L	-	6 L	4 L	4 L	2 L	2 L	-	6 L	3 L	2 L	-
[(L)Ni <sub>2</sub> Cl <sub>2</sub> (EtOH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].2EtOH (4)	3 L	-	2 L	-	4 L	2 L	4 L	2 L	2 L	-	-	-
[(L) <sub>2</sub> Ni <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ].6H <sub>2</sub> O (5)	-	-	2 L	-	3 L	-	4 L	2 L	9 L	5 L	3 L	-
[(HL) <sub>2</sub> Ni <sub>2</sub> (acac) <sub>2</sub> ].7.5H <sub>2</sub> O (6)	-	-	3 L	-	2 L	-	2 L	-	2 L	-	-	-
[(HL) <sub>2</sub> Ni <sub>2</sub> (8-HQ) <sub>2</sub> ].2H <sub>2</sub> O.EtOH (7)	5 L	2 L	11 L	8 L	13 I	9 I	3 L	-	6 L	3 L	-	-
[(L) <sub>2</sub> Ni <sub>2</sub> (Bpy) <sub>2</sub> ].3H <sub>2</sub> O (8)	-	-	5 L	2 L	2 L	-	4 L	2 L	8 L	5 L	-	-
[(L)Ni <sub>2</sub> (OAc) <sub>2</sub> (Phen)(H <sub>2</sub> O) <sub>4</sub> ].0.5H <sub>2</sub> O (9)	4 L	2 L	8 L	6 L	7 L	3 L	4 L	-	5 L	2 L	-	-
[(L)Ni <sub>2</sub> Cl <sub>2</sub> (Phen)(H <sub>2</sub> O) <sub>4</sub> ].3.5H <sub>2</sub> O (10)	10 L	6 L	5 L	2 L	4 L	2 L	5 L	3 L	6 L	4 L	-	-
Control #	35	26	35	25	36	28	38	27	35	28	37	26

\* = Calculated from 3 values.

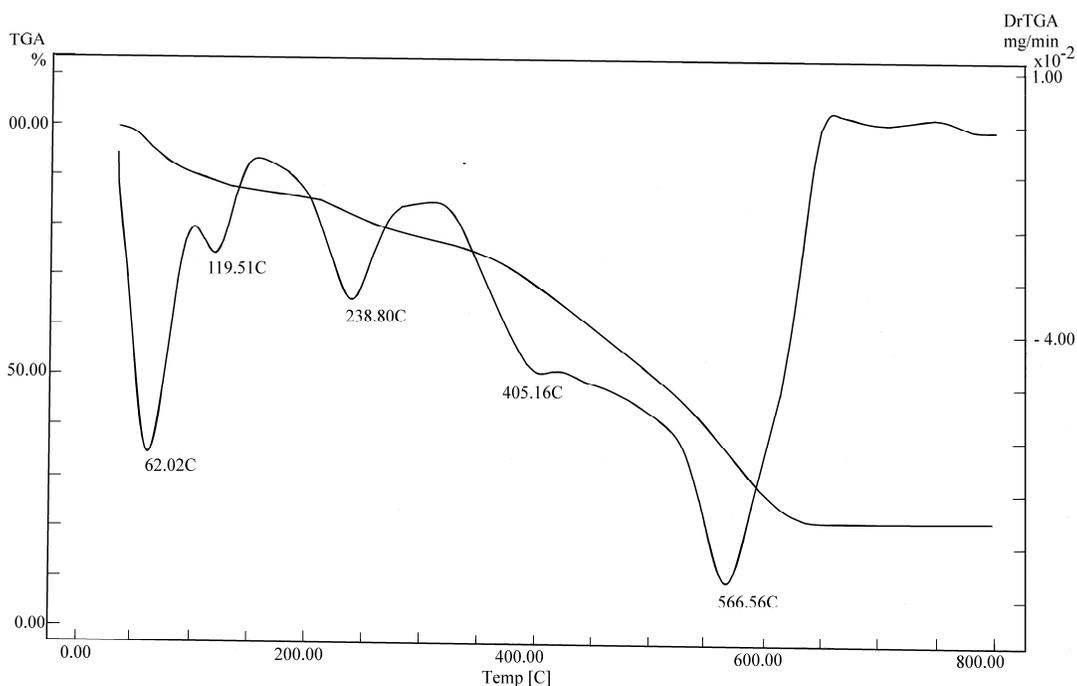
\*\* = identified on the basis of routine cultural, morphological and microscopical characteristics.

- = No effect.

L: Low activity = Mean of zone diameter ≤ 1/3 of mean zone diameter of control.

I: Intermediate activity = Mean of zone diameter ≤ 2/3 of mean zone diameter of control.

#: Chloramphenicol in the case of Gram-positive bacteria, cephalothin in the case of Gram negative bacteria and cycloheximide in the case of fungi.

Fig. 1. TGA/DrTGA of [(L)Ni<sub>2</sub>Cl<sub>2</sub>(Phen)(H<sub>2</sub>O)<sub>4</sub>].3.5H<sub>2</sub>O (complex 10).

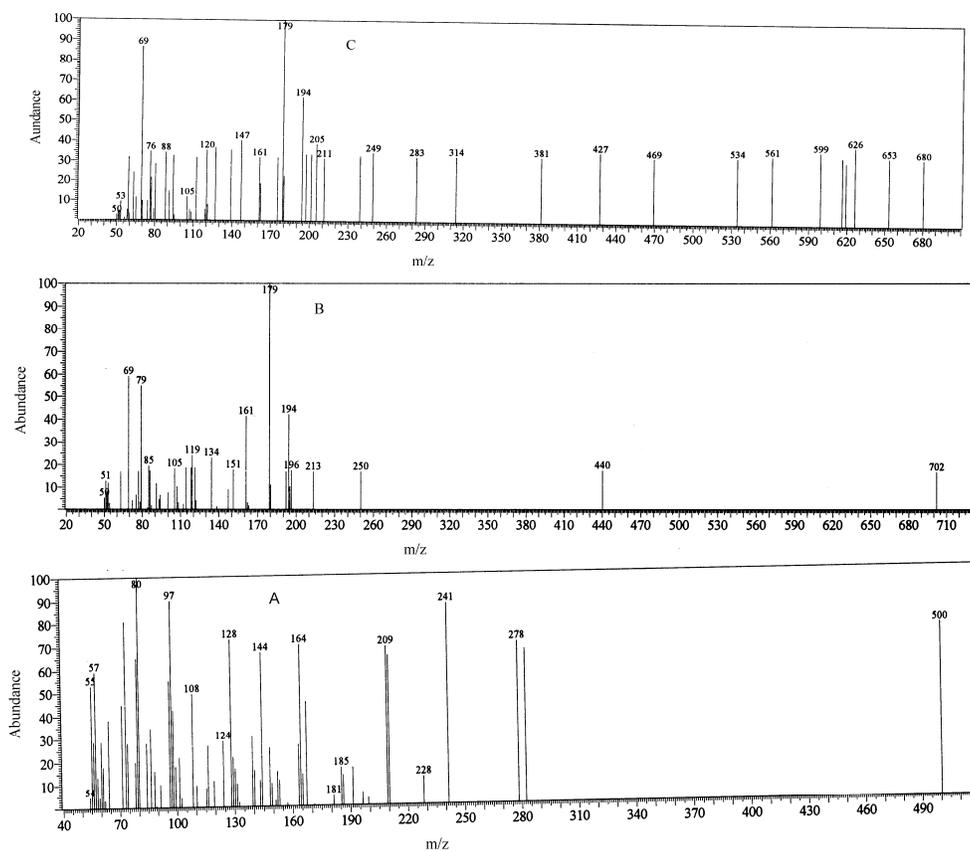


Fig. 2. Mass spectra of the complexes A:  $[(L)Ni_2(OAc)_2(H_2O)_4] \cdot H_2O \cdot 0.5EtOH$  (**2**)  
 B:  $[(HL)_2Ni_2(acac)_2] \cdot 7.5H_2O$  (**6**), and C:  $[(L)Ni_2(OAc)_2(Phen)(H_2O)_4] \cdot 0.5H_2O$  (**9**).

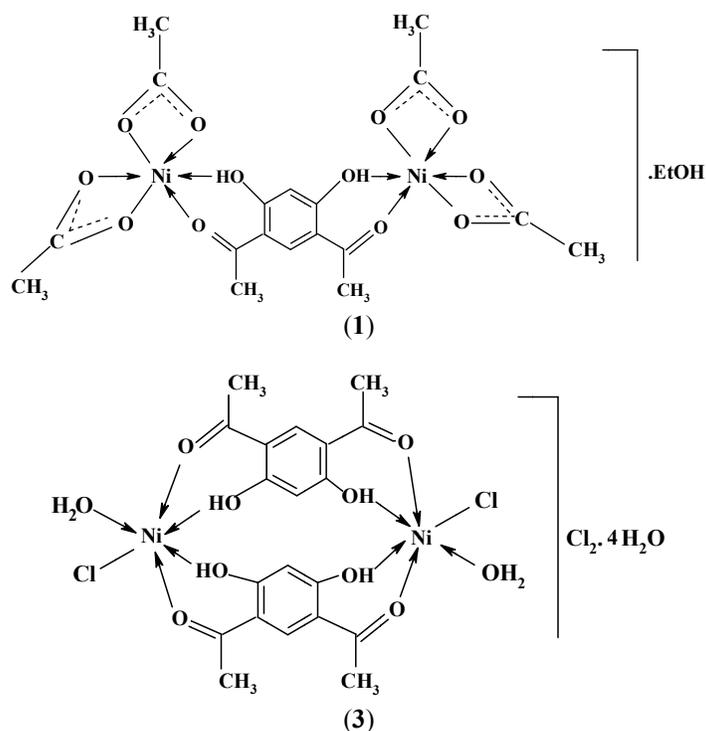


Fig. 3. Representative structures of the binuclear Ni(II) complexes obtained without using LiOH in preparation (**1** and **3**).

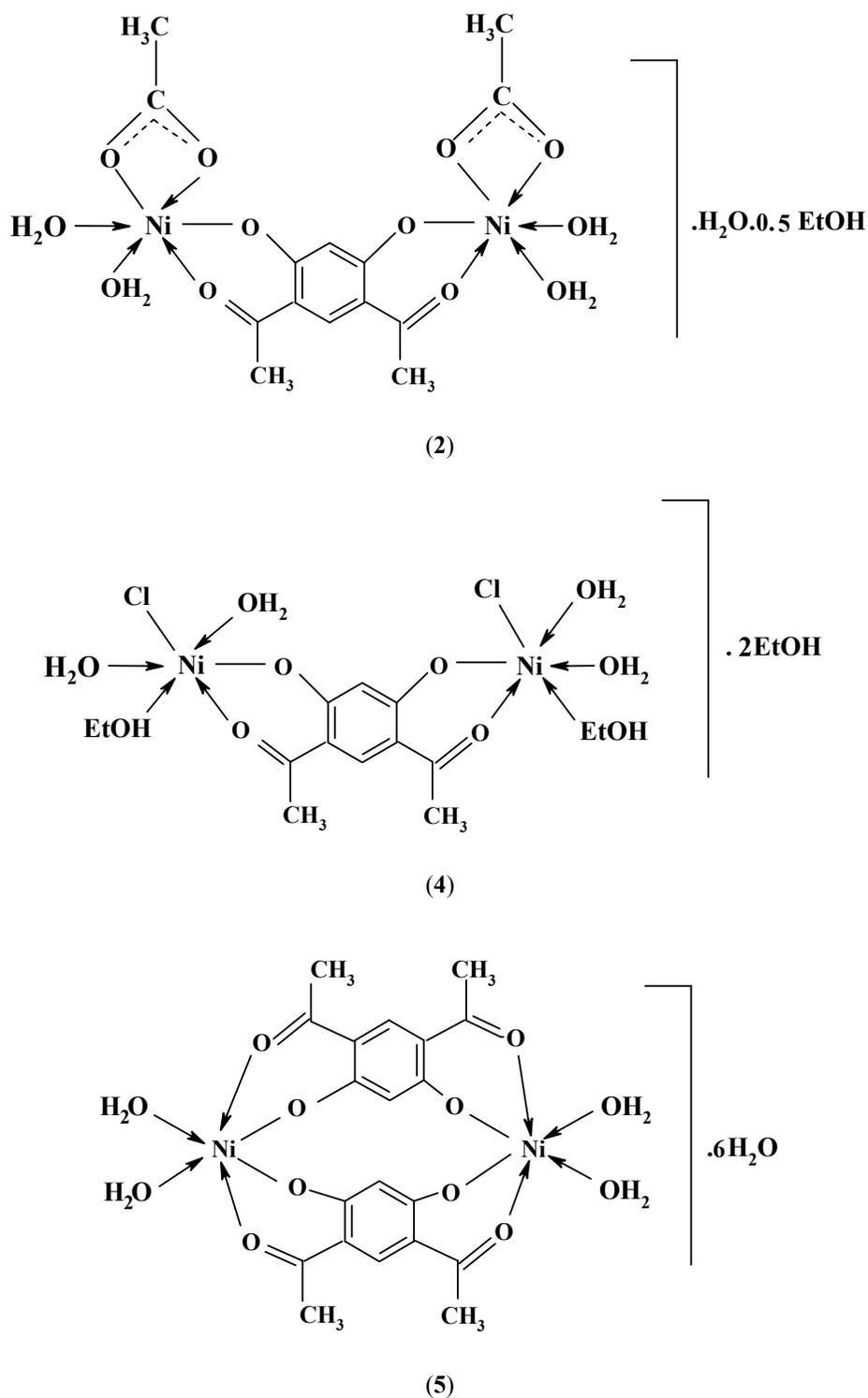
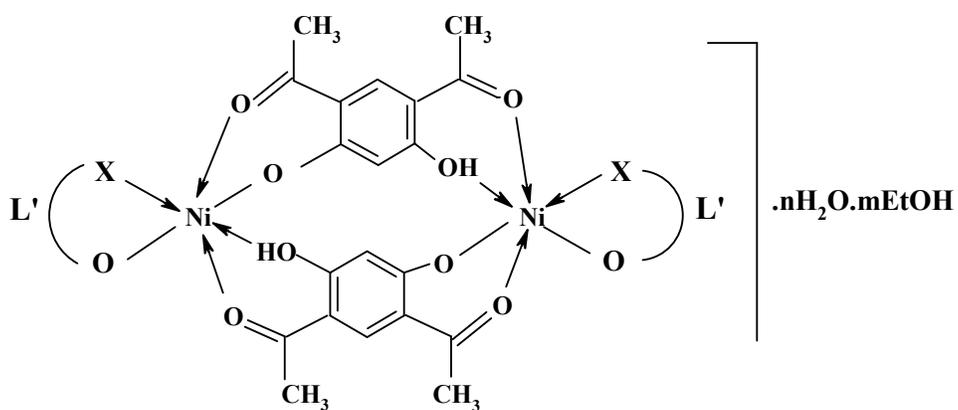
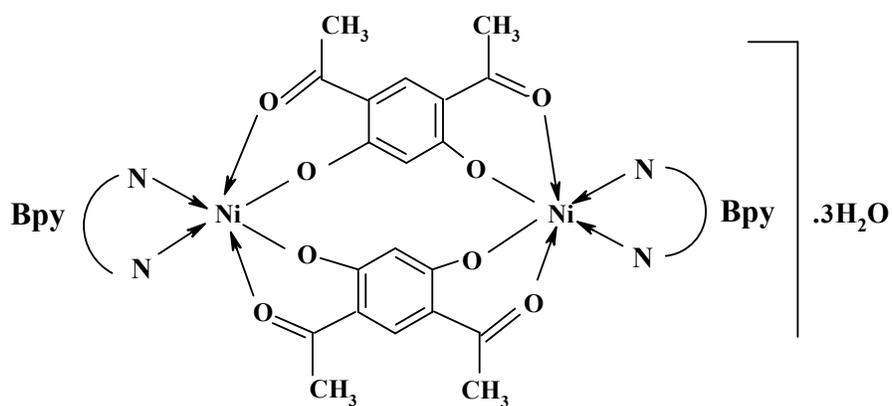


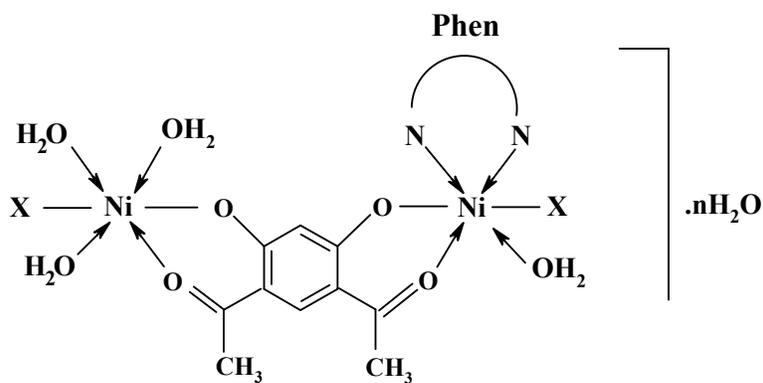
Fig. 4. Representative structures of the binuclear Ni(II) complexes obtained by using LiOH in preparation (2, 4 and 5).



X	n	m	Complex
O	7.5	nil	6
N	2	1	7



(8)



X	n	Complex
OAc	0.5	9
Cl	3.5	10

Fig. 5. Representative structures of the mixed-ligand complexes.

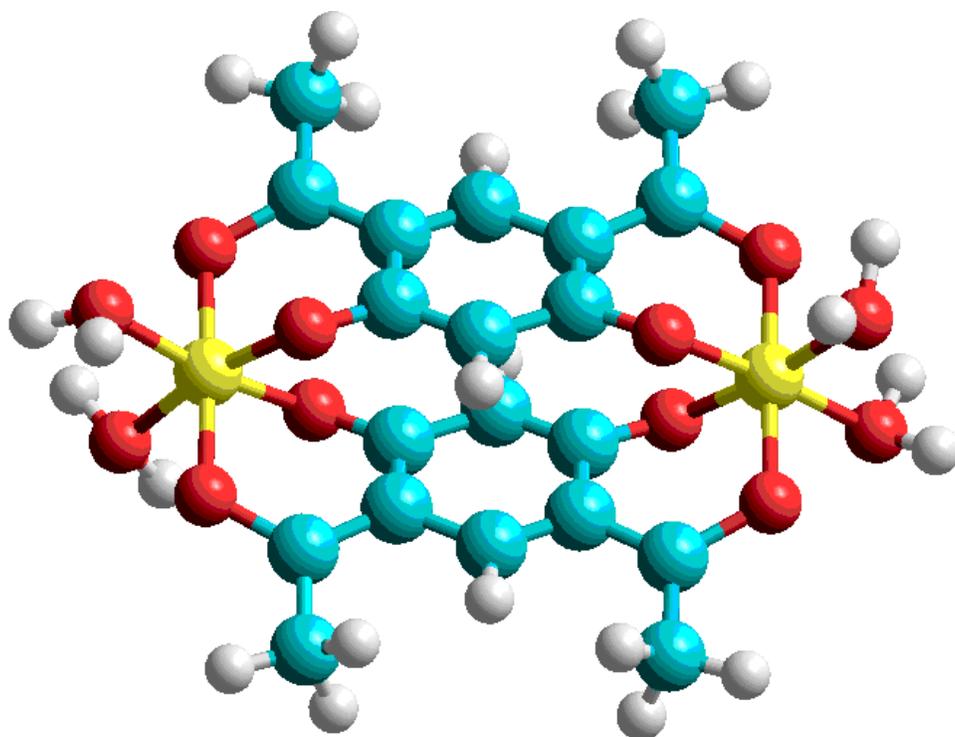
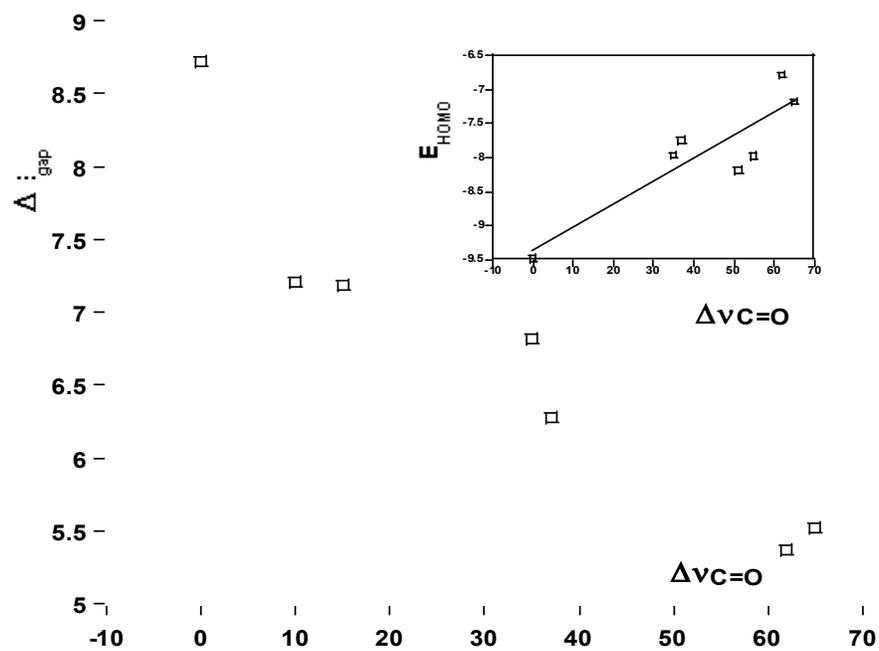


Fig. 6. Optimized structure of complex 5.

Fig. 7. Relation between  $\Delta v(\text{C}=\text{O})$  with  $\Delta E_{\text{gap}}$  ( $\Delta E_{\text{gap}} = E_{\text{Lumo}} - E_{\text{HOMO}}$ ).



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