

Synthesis and characterization of some novel macrocyclic Ni^{II} complexes

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Abstract Novel macrocyclic Ni^{II} complexes were synthesized by the template reactions of different organic dicarbonyls (benzil, 2,3-butanedione and 2,6-diacetylpyridine) with the corresponding aliphatic diamines [ethylene diamine (en), diethylene triamine (tri), triethylene tetraamine (tetr) and tetraethylene pentaamine (pent)] and in the presence of NiCl₂·6H₂O. All the above reactants were mixed together in the same flask using 2+2 technique to form Schiff-base macrocycle complexes. The isolated amorphous macrocyclic Ni^{II} solid complexes have the general formulae, [Ni(L₁)Cl₂]EtOH, [Ni(L₂)Cl₂]1/2EtOH, [Ni₂(L₃)Cl₄], [Ni₂(L₄)Cl₂]Cl₂·2H₂O, [Ni(L₅)Cl₂]6H₂O, [Ni(L₆)Cl₂]3H₂O, [Ni(L₇)Cl₂]4H₂O, [Ni₂(L₈)Cl₂(H₂O)₂]Cl₂, [Ni(L₉)Cl₂]Cl₂, [Ni₂(L₁₀)Cl₄(H₂O)₂], [Ni₂(L₁₁)Cl₂(H₂O)₂]Cl₂ and [Ni₂(L₁₂)Cl₄]2.5H₂O·EtOH. These complexes were characterized using chemical, molar conductance, spectral (UV–Vis, IR, ¹H-NMR, mass), magnetic and thermal measurements. The values of molar conductivities in DMF suggest that the isolated amorphous solid complexes are electrolytic and/or non-electrolytic in nature depending on the type of the synthesized ligand and the number of Ni^{II} ions within the same complex. The IR spectra of all metal complexes indicate that the ligands behave in a tetradentate

manner coordinating via the four azomethine nitrogen's (C=N) or two azomethine nitrogen's and two pyridyl nitrogen's and/or two azomethine nitrogen's and two NH groups, respectively. The values of magnetic for all Ni²⁺ complexes suggest the existence of octahedral geometry around the Ni^{II} ion in the monomeric or in the dimeric forms. In all cases the ligands form five-member rings around the Ni^{II} ions. Also, the results of electronic spectra suggest an octahedral geometry around the Ni^{II} ion. Moreover, the results of thermal studies indicate the mechanism of decomposition as well as the number of EtOH inside and/or outside the coordination sphere. Finally, the isolated solid ligands as well as the synthesized amorphous Ni^{II} complexes have been applied against fungi, bacteria and DNA.

Keywords Macrocyclic complexes · Tetraaza-Schiff-bases complexes · Biological activities

Introduction

Synthetic macrocycles are a growing class of compounds with varying chemistry, wide range of different molecular topologies and acts as donor atoms [1–10]. The chemical properties of macrocyclic complexes can be tuned to force metal ions to adopt unusual coordination geometry. Transition metal macrocyclic complexes have been received much attention as an active part of metalloenzymes [11] as biomimic model compounds [12] due to their resemblance with natural proteins like hemerythrin and enzymes. Also, Schiff-bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. Moreover, it is well known that the Schiff-bases provided a

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foundation stone for the building of contemporary macrocyclic chemistry [13, 14]. A wide Schiff-base macrocycles have evolved from the early studies, many of which involve the use of 2,6-diacetylpyridine and 2,6-diformylpyridine as building blocks. It is possible to find an oligomeric series of macrocycles based on the condensation of these pyridine dicarbonyls with 1,*n*-diaminoalkanes [15, 16] and routes of formation of [1+1] and [2+2] Schiff-base macrocycles. The role of the metal ion in these metal-ion cyclizations is to control the supra-molecular assembly of pre-cyclization fragments, most likely the formation of metal complexes derived from the precursors. The desired cyclization product then results from the intra-molecular interaction in the transition state. It is well known that the size and the ionic potential of the template appear to be important factors in the reaction. In view of the above views, we report herein the synthesis and characterization of some macrocyclic Ni^{II} complexes derived from the reactions of dicarbonyl compounds (benzil, 2,3-butanedione and 2,6-diacetylpyridine) with some diamines (ethylene diamine, diethylene triamine, triethylene tetraamine and tetraethylene pentaamines) in the presence of NiCl₂·6H₂O and mixed solvents. These complexes are characterized by elemental analyses, molar conductance, spectral (IR, UV–Vis, ¹H-NMR, mass), magnetic and thermal measurements. Finally, the macrocyclic ligands and their metal complexes have also been screened against bacteria and DNA.

Experimental

Reagents and apparatus

The Ni^{II} content in the metal complexes was determined by complexometric titration using EBT and/or murexide as indicators [17]. Also, the chloride content was determined gravimetrically as silver chloride [10]. Carbon, hydrogen and nitrogen contents were determined at the Microanalytical Unit, Cairo University, Egypt. Molar conductivities measurements were carried out in DMF and DMSO (10⁻³ M) using Tacussel model CD75 at Mansoura University, Mansoura, Egypt. The IR spectra in the 400–4000 cm⁻¹ range were recorded in KBr and/or Nujol on a Mattson 5000 FTIR Spectrometer at Mansoura University, Egypt. The electronic spectra for the ligands and its Ni^{II} complexes were recorded in Nujol mull in the range (200–900 nm) on a Unicam spectrometer model UV2 at Mansoura University, Egypt. The ¹H-NMR spectra of the ligand were recorded on Jeol-90Q Fourier transform (200 MHz) in d₆-DMSO at Cairo University, Egypt. Magnetic moments (μ_{eff}) were determined using a Sherwood balance at room temperature (25 °C) with Hg[Co(NSC)₄] as a calibrate at Mansoura University. The

diamagnetic corrections for the ligands and the metal atoms were computed using Pascal's constants [18]. Thermal analysis measurements (TGA and DTG) were recorded on a Schimadzu model 50 instrument using 20 mg for the complex. The nitrogen flow and heating rates were 20 cm³ min⁻¹ and 10 °C min⁻¹, respectively. The molecular weights of the ligands were determined using Rast's method [19] while the molecular weights of some Ni²⁺ complexes were recorded on Shimadzu GC-MS-QP 1000 Ex. at 70 eV Spectrometer. The starting dicarbonyl compounds [benzil (Bz), 2,3-butanedione (BD) and 2,6-diacetylpyridine (DAP)] and the aliphatic diamines [ethylene diamine (en), diethylene triamine (tri), triethylene tetraamine (tetra) and tetraethylene pentaamine (pent)] were purchased from Acors, Fluka, Merck and/or Aldrich, respectively, and used without any further purification. Also, the solvents used (EtOH, Et₂O, THF, dioxane, DMF and DMSO) and the nickel chloride hexahydrate (NiCl₂·6H₂O) was of BDH quality.

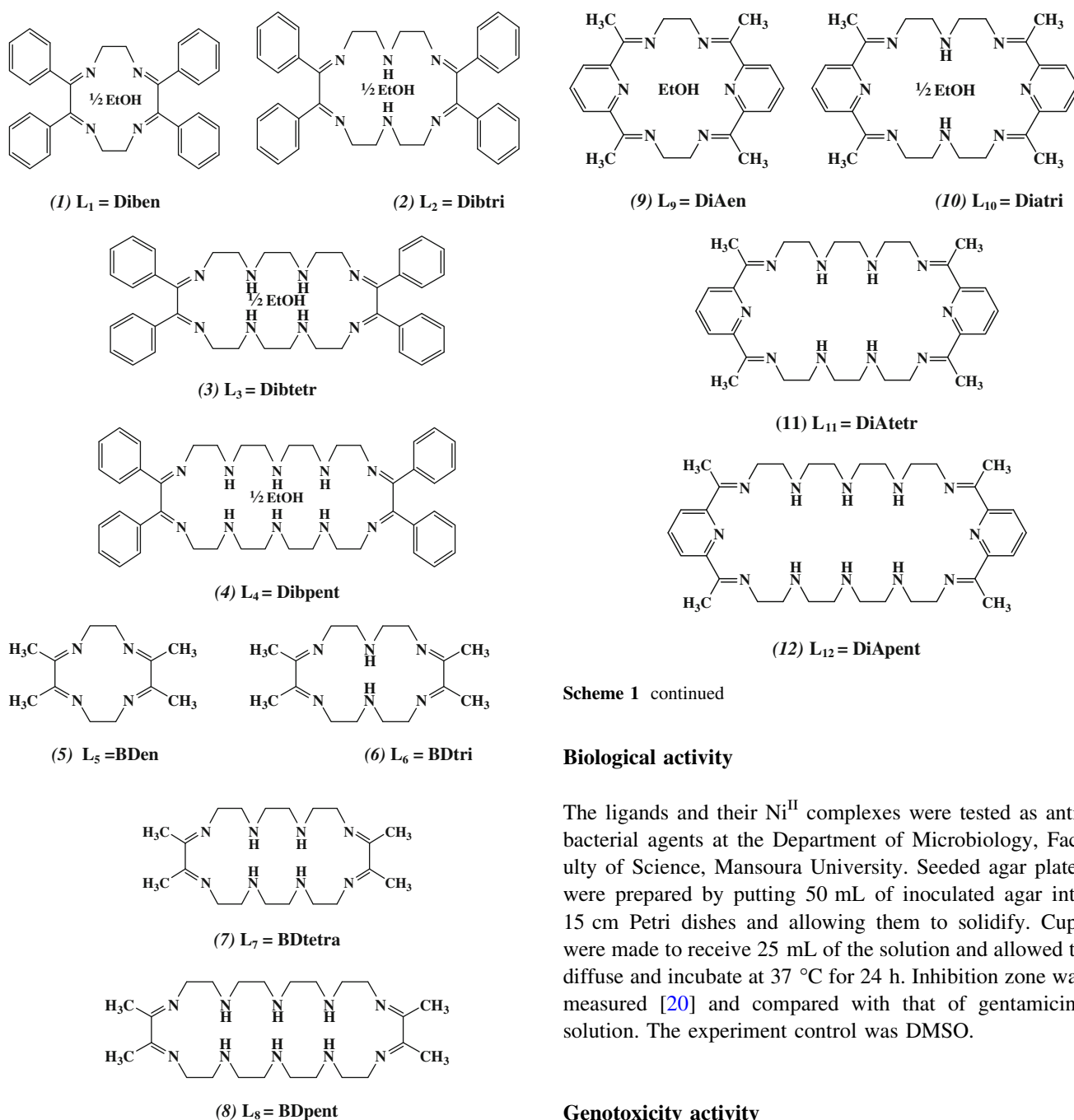
In the genotoxicity activity studies the separation was carried out using electrophoresis of the type SCIE-PLAS and model HU20.

Preparation of the ligands

The macrocyclic ligands under investigation (L₁, L₂, L₃, L₄, L₅, L₆, L₇, L₈, L₉, L₁₀, L₁₁ and L₁₂) were synthesized by the condensation of the dicarbonyls (benzil, 2,3-butanedione and 2,6-diacetylpyridine) with the corresponding aliphatic diamines (en, tri, tetra and penta) in a mixture of solvents (80% THF:20% EtOH and/or 80% dioxane:20% EtOH) using dilution method and the structures of the ligands are represented in Scheme 1. The reaction mixture was held under reflux with stirring for 4–18 h at 60 °C. The time of reflux and the type of solvent used depends on the reactants used for the preparation of the ligands. The isolated amorphous solid macrocyclic ligands were filtered off hot and washed several times with cold EtOH and Et₂O, respectively. The yields of the macrocyclic products (Table 1) are very poor (10–15%) and the products were kept in a desiccator over P₄O₁₀. Since the yields of the isolated ligands by the direct reaction are very poor so the Ni^{II} complexes were synthesized by template reaction.

Synthesis of Ni^{II} complexes

Generally, all the Ni^{II} complexes were synthesized by the reaction of two moles of the dicarbonyls under investigation (benzil, 2,3-butanedione or 2,6-diacetylpyridine) in 300 mL of a mixed solvents (80% THF:20% EtOH or 80% dioxane:20% EtOH) with 2 mol of the aliphatic amines (en, tri, tetra or pent) followed by adding 1 mol of



Scheme 1 continued

Biological activity

The ligands and their Ni^{II} complexes were tested as anti-bacterial agents at the Department of Microbiology, Faculty of Science, Mansoura University. Seeded agar plates were prepared by putting 50 mL of inoculated agar into 15 cm Petri dishes and allowing them to solidify. Cups were made to receive 25 mL of the solution and allowed to diffuse and incubate at 37 °C for 24 h. Inhibition zone was measured [20] and compared with that of gentamicine solution. The experiment control was DMSO.

Genotoxicity activity

A solution of 2 mg of calf thymus DNA was dissolved in 1 mL of sterile doubly distilled water. Stock concentrations of the investigated ligands and their Ni^{II} complexes were prepared by dissolving 2 mg mL^{-1} in DMSO. An equal volume of each compound and DNA were mixed thoroughly and kept at room temperature for 2–3 h. The effect of the chemicals on DNA was analyzed by agarose gel electrophoresis. A 2 mL of loading dye was added to 15 mL of the DNA mixture before being loaded into the well of an agarose gel. The loaded mixtures were fractionated by electrophoresis, visualized by UV and photographed.

Scheme 1 The structures of the isolated ligands

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in the least amount of EtOH. The reaction mixture was refluxed on a hot plate at 60 °C for 2 h. This procedure promotes of formation of mono or binuclear macrocycle complex of the type [2+2]. The isolated amorphous Ni^{II} complexes were filtered off hot followed by washing with cold solutions of EtOH and Et_2O , respectively. The products were kept in a desiccator over P_4O_{10} . The yields of the isolated Ni^{2+} complexes fall in the 54–60% range as shown in Table 2.

Results and discussion

All the macrocycle Schiff-base ligands under investigation were prepared in a very poor yield (10–15%) and hence the Ni^{II} complexes were not isolated by the direct method i.e., by the reaction of the isolated ligand with the Ni²⁺ salt, but prepared by template techniques. The chemical analyses for the isolated organic macrocyclic Schiff-base ligands are recorded in Table 1. The results of elemental analyses together with the spectral (IR, ¹H-NMR and mass) and thermal measurements suggest the existence of 1/2 or one molecule of EtOH inside some of the isolated ligands i.e., L₁ (1), L₂ (2), L₃ (3), L₄ (4), L₉ (9) and L₁₀ (10) while the other remaining ligands [L₅ (5), L₆ (6), L₇ (7), L₈ (8), L₁₁ (11) and L₁₂ (12)] does not contain any solvent molecules. The structures of the isolated ligands are represented in Scheme 1.

The ethanol molecule is more likely reside inside the cavity of some of the macrocyclic ligands and is probably forms a type of intra-molecular hydrogen bonding with the internal donor groups (C=N or the NH) existed in the cavity of the macrocyclic ligand. The analytical and some physical results for the isolated solid Ni^{II} complexes are listed in Table 2. All the Ni^{II} complexes are varied in colors (greenish-blue, brown and/or black), stable in air for more than 2 months and after which the complexes are polymerized and decomposed. Also, the complexes are insoluble in most common organic solvents but freely soluble in DMSO or DMF. The values of molar conductivities in DMF at 25 °C for the Ni^{II} complexes fall in the 2.8–80.6 Ω⁻¹ cm² mol⁻¹ range (Table 2) indicating the non-electrolytic nature for the complexes having lower conductance values while the higher conductance values

(80.1–80.6 Ω⁻¹ cm² mol⁻¹) suggest the electrolytic nature of these complexes [21] in DMF as shown in Table 2. On the other hand, the values of molar conductivities in DMSO at 25 °C for the Ni(II) complexes fall in the 1.1–42.4 Ω⁻¹ cm² mol⁻¹ range (Table 2). The high values (40.9–42.4 Ω⁻¹ cm² mol⁻¹) suggest the electrolytic nature of these complexes [21]. It is worth mentioning that the comparatively high values of molar conductance in DMF are higher than these in DMSO is mainly due to the strong donor capacity of DMF. Moreover, the results show that the metal complexes have melting points fall in the 100–290 °C range (Table 2). This suggests the existence of weak bond between the Ni^{II} ion and the ligands. Also, this explains the tendency of the Ni²⁺ complexes to polymerize and decompose on leaving these complexes in air.

The IR spectra of the ligands and their Ni^{II} complexes are carried out in KBr and/or Nujol. The IR spectra of the free ligands derived from benzil (L₁, L₂, L₃ and L₄) show a strong band in the 3460–3422 cm⁻¹ region assigned to ν(OH) vibration. This band is disappeared on heating the four ligands in an oven at 120 °C for 2 h due to the removal of the solvent molecule. All the ligands with low melting points than 180 °C (Table 1) were dried in a drying pistol under reduced pressure. Also, the two bands observed in the 3317–3289 and 1662–1572 cm⁻¹ regions are attributed to ν(NH) and ν(C=N) vibrations [22, 23], respectively. The obscure of the first band in the first ligand (L₁) indicates that this ligand does not contain NH band. Moreover, the appearance of the azomethine group together with the obscure of the carbonyl together with the appearance of the (C=N) groups proves that the condensation between NH₂ and CO groups has been occurred. The data of ¹H-NMR spectra of the ligands (L₁, L₂, L₃ and L₄)

Table 1 Analytical data and some physical properties of the macrocyclic ligands

Compound	Color	M.Wt ^a	Yield %	M.P. (°C)	Found (calcd.) (%)		
					C	H	N
L ₁ = Diben = C ₃₂ H ₂₈ N ₄ ·1/2EtOH	White	485 (491.6)	15	158 (d)	(80.6) 80.4	(6.4) 6.2	(11.4) 10.9
L ₂ = Dibtri = C ₃₆ H ₃₈ N ₆ ·1/2EtOH	White	570 (577.8)	14	160–162 (d)	(76.9) 76.4	(7.2) 6.8	(14.6) 14.3
L ₃ = Dibtetr = C ₄₀ H ₄₈ N ₈ ·1/2EtOH	Pale yellow	661 (663.9)	12	157(d)	(74.2) 73.8	(7.7) 7.5	(16.9) 16.3
L ₄ = Dibpent = C ₄₄ H ₅₈ N ₁₀ ·1/2EtOH	Orange	741 (750.1)	10	75 (d)	(72.1) 71.8	(8.2) 8.1	(18.7) 18.3
L ₅ = BDen = C ₁₂ H ₂₀ N ₄	Black	212 (220.3)	14	150 (d)	(65.4) 65.1	(9.2) 8.8	(25.4) 25.3
L ₆ = BDtri = C ₁₆ H ₃₀ N ₆	Orange	298 (306.5)	14	160 (d)	(62.7) 62.5	(9.9) 9.6	(27.4) 26.9
L ₇ = BDtetr = C ₂₀ H ₄₀ N ₈	Brown	389 (392.6)	11	115 (d)	(61.2) 60.8	(10.3) 10.0	(28.5) 28.2
L ₈ = BDpent = C ₂₄ H ₅₆ N ₁₀	Brown	471 (478)	10	125 (d)	(60.2) 59.6	(10.5) 10.0	(29.3) 29.1
L ₉ = DiAen = C ₂₂ H ₂₆ N ₆ ·EtOH	Yellow	416 (420.6)	13	157(d)	(68.5) 68.1	(7.7) 7.3	(20.0) 19.8
L ₁₀ = DiAtri = C ₂₆ H ₃₆ N ₈ ·1/2EtOH	Orange	477 (483.7)	14	75 (d)	(67.1) 66.8	(8.1) 7.8	(17.4) 16.9
L ₁₁ = DiAtetr = C ₃₀ H ₄₆ N ₁₀	Black	538 (546.8)	10	124 (d)	(65.9) 65.6	(8.5) 8.1	(25.6) 25.2
L ₁₂ = DiApent = C ₃₄ H ₅₆ N ₁₂	Orange	627 (632.9)	10	90 (d)	(64.5) 64.2	(8.9) 8.4	(26.6) 26.2

d decomposed

^a Determined by Rast's method

Table 2 Analytical data and some physical properties of the isolated metal complexes

Compound	Color	M.P. (°C)	Yield %	C	Calcd. (found) (%)				X (Cl: I)	Λ (Ω^{-1} cm ² mol ⁻¹) in DMF (DMSO)	μ_{eff}	M.Wt ^a
					H	N	M					
[Ni(L ₁)Cl ₂]EtOH	Brown	290 (d)	60	63.4 (63.0)	5.3 (5.1)	8.7 (8.3)	9.1 (8.6)	11.0 (10.6)	4.5 (1.8)	3.01	644.3 (642) ^a	
[Ni(L ₂)Cl ₂]1/2EtOH	Greenish-blue	205 (d)	58	62.8 (62.7)	5.8 (5.5)	11.9 (11.7)	8.3 (8.2)	10.0 (9.9)	3.8 (1.2)	2.79	—	
[Ni ₂ (L ₃)Cl ₄]	Brown	180 (d)	54	53.4 (53.2)	5.4 (5.2)	12.5 (12.2)	13.1 (13.0)	15.8 (15.3)	5.5 (2.4)	3.00	—	
[Ni ₂ (L ₄)Cl ₂]Cl ₂ ·2H ₂ O	Reddish-brown	100 (d)	50	51.7 (51.4)	6.1 (5.9)	13.7 (13.4)	11.5 (11.2)	13.9 (13.6)	80.2 (41.1)	2.86	1022 (1017) ^b	
[Ni(L ₅)Cl ₂]6H ₂ O	Brown	130 (d)	59	31.5 (31.0)	7.0 (7.1)	12.2 (12.1)	12.8 (12.7)	15.5 (15.1)	2.8 (1.1)	2.90	458 (446) ^a	
[Ni(L ₆)Cl ₂]3H ₂ O	Brown	135 (d)	59	39.2 (39.2)	7.4 (7.2)	17.2 (16.8)	12.0 (11.8)	14.5 (14.3)	2.9 (1.6)	1.58	490.1 (489)	
[Ni(L ₇)Cl ₂]4H ₂ O	Brown	100 (d)	56	40.4 (40.3)	8.1 (8.0)	18.9 (18.6)	9.9 (9.5)	11.9 (11.6)	4.2 (2.3)	2.77	594.3 (588) ^b	
[Ni ₂ (L ₈)Cl ₂ (H ₂ O) ₂]Cl ₂	Brown	100 (d)	50	37.2 (37.1)	7.0 (6.9)	18.1 (17.7)	15.2 (14.9)	18.3 (18.1)	80.6 (42.4)	2.97	774 (766) ^b	
[Ni(L ₉)Cl ₂]	Brown	140 (d)	60	52.4 (51.8)	5.6 (5.3)	15.9 (15.7)	11.1 (10.9)	13.5 (13.2)	3.8 (1.4)	2.88	—	
[Ni ₂ (L ₁₀)Cl ₄ (H ₂ O) ₂]	Bluish-green	205 (d)	60	41.3 (41.1)	5.3 (5.2)	14.8 (14.4)	15.5 (15.1)	18.8 (18.3)	3.9 (1.4)	2.91	—	
[Ni ₂ (L ₁₁)Cl ₂ (H ₂ O) ₂]Cl ₂	Brown	180 (d)	55	42.8 (42.6)	6.0 (5.5)	16.6 (16.4)	14.0 (13.6)	16.8 (16.5)	80.1 (40.9)	2.84	—	
[Ni ₂ (L ₁₂)Cl ₄]2.5H ₂ O·EtOH	Black	115 (d)	51	43.9 (43.0)	6.9 (6.3)	17.1 (17.3)	11.9 (12.2)	14.4 (14.6)	7.7 (4.1)	2.89	983 (977) ^b	

^d decomposed^a Determined by mass spectrometer, ^b determined by Rast's method

in d₆-DMSO is taken as additional evidence for the disappearance of the NH₂ group due to the condensation of the carbonyl group with the formation of the azomethine group [24]. The results are recorded in Table 3. The electronic spectra of the ligands in DMSO show two main bands in the 250–400 nm range assigned to the $\pi \rightarrow \pi^*$ transitions in the C=C and C=N groups [25, 26]. The positions of these bands are differing from the observed values in the electronic spectra of benzil and aliphatic amines confirming the obscure of the carbonyl together with the appearance of the azomethine group [24]. The observation of a new band at ~ 385 nm is mainly assigned to the $n \rightarrow \pi$ transition of the C=N group.

The IR spectra of the ligands derived from 2,3-butanedione (L₅, L₆, L₇ and L₈) show the obscure of the band above 3400 cm⁻¹ due to $\nu(\text{OH})$ vibration. This behavior is totally differ from the above mentioned ligands (L₁, L₂, L₃ and L₄) which shows the $\nu(\text{OH})$ vibration. This suggests the absence of any solvent inside the cavity of these ligands (L₅, L₆, L₇ and L₈). Also, the spectra exhibit a band in the 1626–1648 cm⁻¹ range assigned to the C=N group. Moreover the band observed in the 3350–3290 cm⁻¹ is assigned to $\nu(\text{NH})$ vibration. The results of the ¹H-NMR spectra in d₆-DMSO are shown in Table 3. The electronic spectra of the ligands (L₅, L₆, L₇ and L₈) show a new band at ~ 400 nm assigned to the $n \rightarrow \pi$ transition of the C=N group.

Finally, the ligands derived from the condensation of 2,6-diacetylpyridine with the aliphatic amines under investigation (L₉, L₁₀, L₁₁ and L₁₂) show the existence of a strong band in the IR spectra, for the first two ligands (L₉ and L₁₀), at ~ 3430 cm⁻¹. This band is assigned to $\nu(\text{OH})$ vibration due to the existence of EtOH inside the cavity of the macrocyclic ligand as discussed earlier. The absence of this band in the latter two ligands (L₁₁ and L₁₂) proves the disappearance of EtOH within the cavity of the latter two ligands. It worth mentioning indicates that on drying the ligands containing EtOH in a drying pistol under reduced pressure °C for 4 h, the ethanol molecule was lost. Also, the absence of the NH₂ signal in the ¹H-NMR spectra of the four ligands is taken as evidence for the complete reaction between the carbonyl and the NH₂ groups with the formation of azomethine group. The carbonyl band at ~ 1704 cm⁻¹ in the IR spectrum of 2,6-diacetylpyridine assigned to the carbonyl group was also disappeared on condensation with NH₂ group to form the azomethine group. Also, the two bands observed in the 3345–3300 and 1655–1540 cm⁻¹ regions are attributed to $\nu(\text{NH})$ and $\nu(\text{C}=\text{N})$ vibrations [22, 23], respectively. The electronic spectra of the free ligands (L₉, L₁₀, L₁₁ and L₁₂) in DMF show only one new band at ~ 398 nm assigned to the $n \rightarrow \pi$ transition of the C=N group. Also, the spectra show the characteristic bands assigned to the C=C and C=N bands of the pyridine moiety.

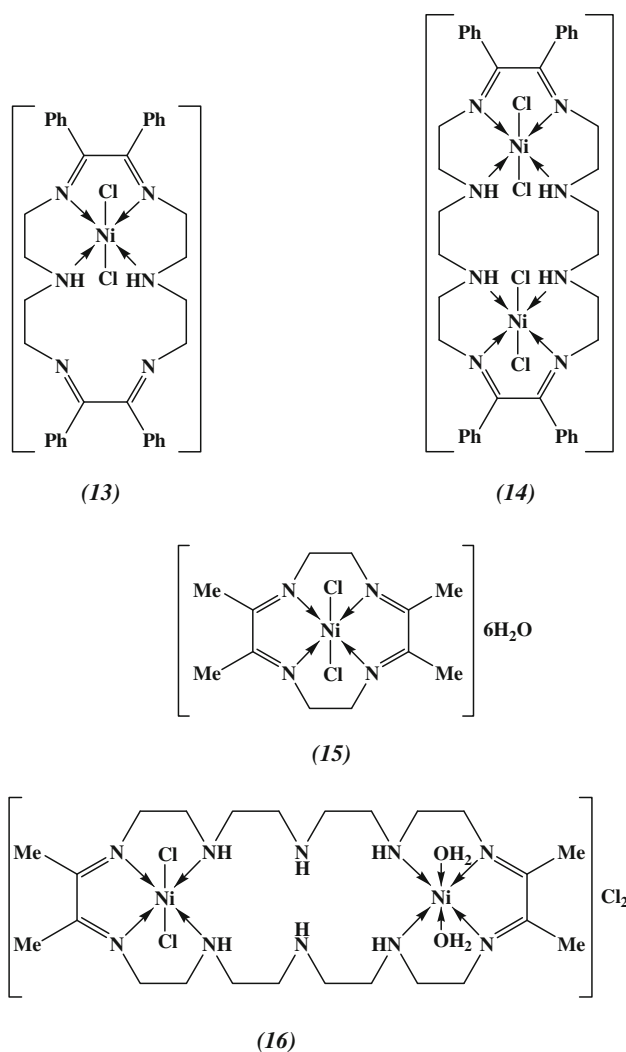
Table 3 The most important assignments of the protons in the free ligands

Ligand	$\delta(\text{CH}_2)$	$\delta(\text{NH})$	$\delta(\text{C}_6\text{H}_5)$	$\delta(\text{CH}_3)$	$\delta(\text{Py})$
L ₁	3.4	–	7.24–7.37	–	–
L ₂	2.49–2.99 3.19–3.38 3.79–4.05	7.84	7.03–7.48	–	–
L ₃	2.36–4.12	7.68	7.17–7.52	–	–
L ₄	3.56	8.7	7.14–7.94	–	–
L ₅	2.7–4.6	–	–	–	–
L ₆	2.8–4.8	7.89	–	–	–
L ₇	2.7–4.9	7.92	–	–	–
L ₈	2.7–5.0	7.56	–	–	–
L ₉	4.82	–	–	2.72	8.18
L ₁₀	4.69	8.79	–	2.61	8.19
L ₁₁	4.78	8.83	–	2.84	8.33
L ₁₂	4.71	8.80	–	2.77	8.26

On comparing the IR spectra of the Ni^{II} complexes with the corresponding free ligands, we observed that the azomethine groups in the ligands are shifted to lower wavenumbers in all complexes suggesting the participation of this group in bonding. The azomethine groups in the free ligands are observed in the 1648–1678 cm⁻¹ range which are shifted to lower wave-numbers in case of the Ni^{II} complexes and observed in the range 1550–1590 cm⁻¹. Also, the IR spectra of the Ni^{II} complexes indicates the participation of the azomethine groups and/or the azomethine and the NH groups in coordination in case of the ligands derived from benzil and/or 2,3-butanedione derivatives. The modes of bonding in some Ni^{II} complexes, derived from benzil and 2,3-butanedione with the different aliphatic amines, are represented by structures 13–16 in Scheme 2.

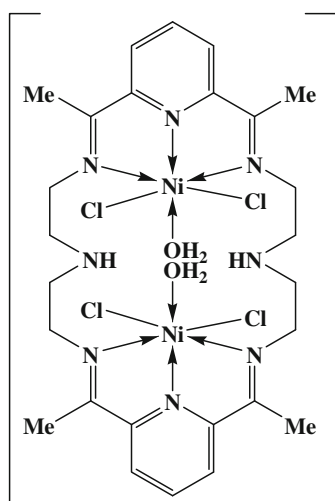
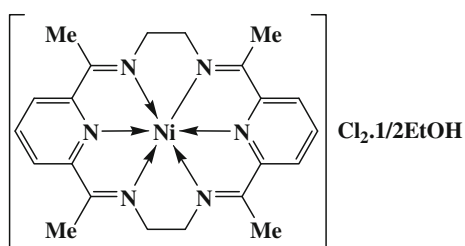
On the other hand the IR spectra of the ligands, derived from 2,6-diacetylpyridine, show the participation of the azomethine alone or the azomethine and the NH groups or the azomethine and the pyridyl nitrogen groups depending on the nature of the ligand or the number of the nickel ions existing inside the cavity of the complex. The structures of some Ni^{II} complexes are represented by structures 17 and 18 as shown in Scheme 3.

The electronic spectra as well as the magnetic moments of the Ni^{II} complexes (Tables 2, 4) suggest the existence of an octahedral around the Ni^{II} ion. The values of magnetic moments fall in the 2.75–3.01 B.M. range indicating the existence of an octahedral geometry around the two Ni^{II} ions. Also, the electronic spectra for all Ni^{II} complexes in DMF show two main bands in the 29940–24876 and 19763–11600 cm⁻¹ regions assigned to ³A_{2g} → ³T_{1g} (³P,

**Scheme 2** The structure of the complexes derived from 2,3-butanedione and benzil

v_3) and ³A_{2g} → ³T_{1g} (³F, v_2) transitions [27], respectively, in octahedral geometry around the two Ni^{II} ion. The ligand field parameters [21–23] are collected in Table 4. The values of the first transition assigned to ³A_{2g} → ³T_{2g} (v_1) transition was calculated as reported earlier [28–30] and are collected in Table 4. This band was obscured in the electronic spectra of the complexes due to the lack of the instrument for measurements in the near IR region. Also, the values of B and β were calculated and collected in Table 4. Moreover, the molecular extinction coefficient (ϵ) for the Ni²⁺ complexes were determined and recorded in Table 4. The low of these values is taken as strong evidence for the existence of octahedral geometry around the Ni²⁺ ion.

The amounts of solvents (EtOH and/or H₂O) inside and outside the coordination sphere were determined using thermal analysis measurements (TGA and DTG), in the 25–400 °C, as well as by gravimetric methods. The results



Scheme 3 The structures of the complexes derived from 2,6-diacetylpyridine

showed that the hydrated solvents (outside the coordination sphere) were removed in the 120–140 °C range while the coordinated solvents were removed above 150 °C. The TGA curve of the Ni²⁺ complex with the general formula, [Ni(L₁)Cl₂]EtOH, is shown in Fig. 1.

The results of mass spectra of the free ligands and the Ni²⁺ complexes are taken as evidence for the formation of 2+2 structures. The values of molecular weights by Rast's method and by mass spectrometer are recorded in Tables 1 and 2. The mass spectrum of the complex with the general formula, [Ni(L₅)Cl₂]6H₂O, is shown in Fig. 2.

The antimicrobial activities of the Ni^{II} complexes against *B. subtilis* and *P. aeruginosa* were studied in details. Growth inhibition zones are directly proportional to the antimicrobial activity of the Ni^{II} complexes. The data suggest that the Gram positive and Gram negative bacteria were affected by the Ni^{II} complexes under investigation. The effects of the genotoxicity on the DNA for the Ni^{II} complexes in comparison to the control sample indicate interesting results. The pictures indicate that the electrophoretic mobility shifts and the tailing of DNA in any lane are indicative of degradation of the calf thymus. The degradation powers of the tested Ni^{II} complexes on calf thymus DNA are high for all complexes supporting the selective action of the Ni^{II} complexes against bacteria and the human or related eukaryotic organisms.

Conclusion

The importance of macrocyclic compounds promotes us to continue this subject and isolate new Ni^{II} complexes. The Ni^{II} complexes derived from the reactions of dicarbonyls (benzil, 2,3-butanedione and 2,6-diacetylpyridine) with some aliphatic amines (en, tri, tet and pent) have been synthesized and characterized by conventional chemical, physical and spectral measurements. The ligands under investigation coordinates in a tetradentate manner via the azomethin (C=N) or NH and C=N groups as in the ligands derived from benzil and 2,3-butanedione. On the other

Table 4 Electronic spectra and ligand field parameters of Ni²⁺ complexes

Complex	ϵ^a	ν_1	ν_2	ν_3	ν_3/ν_2	B_{complex}	$\beta = B_{\text{complex}}/B_{\text{Ni}}$
[Ni(L ₁)Cl ₂]EtOH	6.6	9221	15,015	25,126	1.67	832	0.80
[Ni(L ₂)Cl ₂]1/2EtOH	15	106,656	16,393	25,510	1.56	662	0.64
[Ni ₂ (L ₃)Cl ₄]	9.3	11,033	17,361	27,473	1.58	782	0.75
[Ni ₂ (L ₄)Cl ₂]Cl ₂ ·2H ₂ O	10.8	13,366	19,763	29,940	1.51	640	0.62
[Ni(L ₅)Cl ₂]6H ₂ O	12.1	10,562	17,007	27,778	1.63	873	0.84
[Ni(L ₆)Cl ₂]3H ₂ O	16.9	9860	15,873	25,773	1.62	804	0.77
[Ni(L ₇)Cl ₂]4H ₂ O	8.6	8668	14,286	24,876	1.74	877	0.84
[Ni ₂ (L ₈)Cl ₂ (H ₂ O) ₂]Cl ₂	6.4	8345	14,085	26,455	1.88	1033	0.99
[Ni(L ₉)Cl ₂]Cl ₂ ·3H ₂ O	4.8	10,349	16,667	27,322	1.64	863	0.83
[Ni ₂ (L ₁₀)Cl ₄ (H ₂ O) ₂]	2.9	8389	11,601	26,738	2.30	876	0.84
Ni ₂ (L ₁₁)Cl ₂ (H ₂ O) ₂]Cl ₂	7.8	8945	13,928	27,322	1.96	961	0.92
[Ni ₂ (L ₁₂)Cl ₄]2.5H ₂ O·EtOH	14.4	10,100	16,556	27,624	1.67	925	0.89

^a $\epsilon = 1 \text{ mol}^{-1} \text{ cm}^{-1}$

Fig. 1 Mass spectrum of $[\text{Ni}(\text{L}_3)\text{Cl}_2]6\text{H}_2\text{O}$

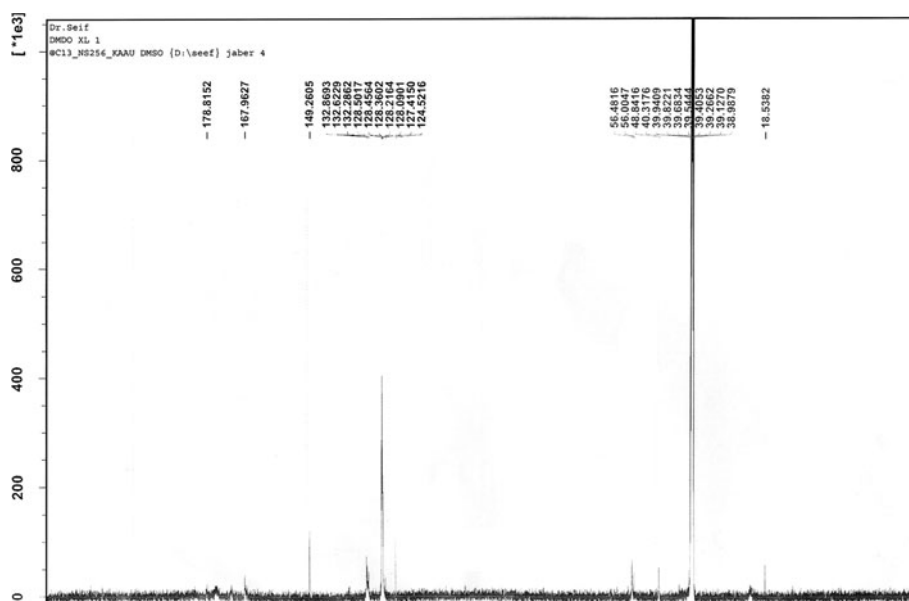
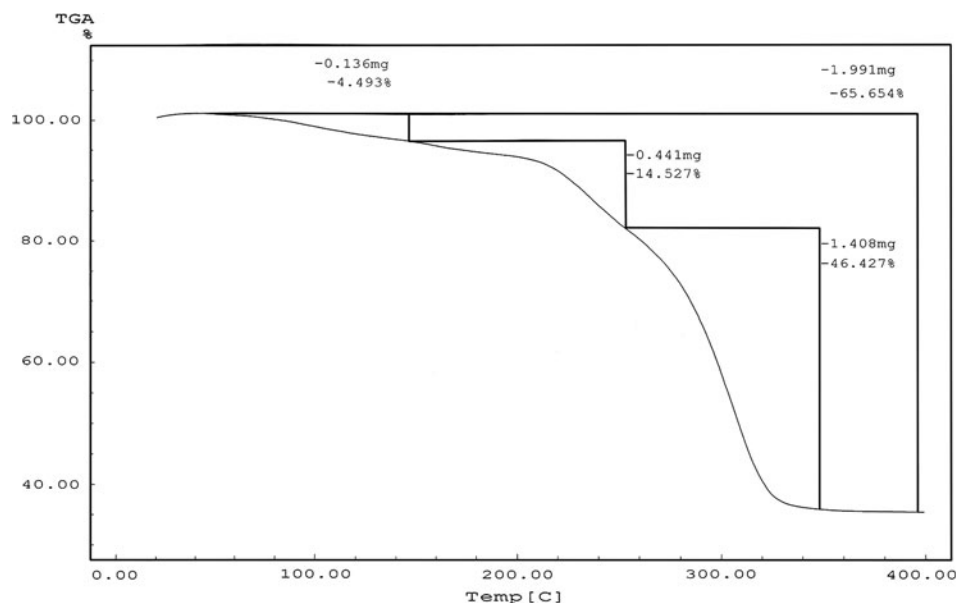


Fig. 2 TGA of the $[\text{Ni}(\text{L}_1)\text{Cl}_2]\text{EtOH}$



hand, the ligands derived from 2,6-diacetylpyridine coordinate in a bidentate manner via the C=N and pyridyl nitrogen groups or in a tridentate manner via the C=N, NH and pyridyl nitrogen groups. The stereochemistry of the isolated Ni^{II} complexes was characterized by using conductance, chemical, spectral, magnetic and thermal analysis measurements. Also, one of our goals is to study the antimicrobial activities of the Ni^{II} complexes against *B. Subtillis* and *P. Aeurginosa*. The data suggest that the Gram positive and Gram negative bacteria were affected by the Ni^{II} complexes under investigation. Moreover, the effects of the genotoxicity on the DNA for the Ni^{II} complexes in comparison to the control sample indicate interesting

results. The degradation powers of the tested Ni^{II} complexes on calf thymus DNA are high for all complexes supporting the selective action of the Ni^{II} complexes against bacteria and the human or related eukaryotic organisms.

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