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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsrt20</u>

Spectral, Magnetic, Thermal, and DNA Interaction of Ni(II) Complexes of Glutamic Acid Schiff Bases

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To cite this article: A. S. Orabi, A. M. Abbas & S. A. Sallam (2013): Spectral, Magnetic, Thermal, and DNA Interaction of Ni(II) Complexes of Glutamic Acid Schiff Bases, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 43:1, 63-75

To link to this article: <u>http://dx.doi.org/10.1080/15533174.2012.684260</u>

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Spectral, Magnetic, Thermal, and DNA Interaction of Ni(II) Complexes of Glutamic Acid Schiff Bases

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Ni(II) complexes with Schiff bases obtained by condensation of glutamic acid with salicylaldehyde; 2,3-; 2,4-; and 2,5dihydroxybenzaldehyde; and o-hydroxynaphthaldehyde have been synthesized using the template method in ethanol or ammonia media. They were characterized by elemental analyses, conductivity measurements, magnetic moment, UV, IR, and ¹H NMR spectra as well as thermal analysis (TG, DTG, DTA). The Schiff bases are dibasic tridentate or tetradentate donors and the complexes have square planar and octahedral structures. The complexes decompose in two or three steps where kinetic and thermodynamic parameters of the decomposition steps were computed. The interactions of the formed complexes with FM-DNA were monitored by UV and fluorescence spectroscopy.

Keywords FM-DNA interaction, glutamic acid Schiff bases, magnetic, Ni(II) complexes, spectral and thermal properties

INTRODUCTION

Several structural studies have been carried out on transition metal complexes of the Schiff bases derived from condensation of salicylaldehyde and hydroxynaphthaldehyde with amino acids in view of the fact that these complexes can be used as non-enzymatic models analogous to the key intermediates in many metabolic reactions of amino acids such as transamination, decarboxylation, α - and β -elimination, racimization, and intermediate products in biologically important reactions.^[1–5] Derivatives of amino acids and pyridoxal or salicylaldehyde Schiff bases have been widely studied as a model systems for studying enzymatic processes.^[6]

A series of N-salicylaldeneglutamatocopper(II) complexes of composition Cu(sal-glu)X, where sal-glu represents Schiff bases derived from salicylaldehyde with L- and DL-glutamic acid and X = pyridine, 2-, 3-, and 4-methylpyridine, were prepared and characterized.^[7] Recently, manganese complexes of the Schiff base derived from 2-hydroxy-1-naphthaldehyde and glutamic acid have been prepared.^[8] We have been interested in the coordination chemistry of Cu(II), Ni(II), Co(II), UO₂²⁺,^[9,10] and lanthanide^[11–13] complexes containing Schiff base ligands derived from glycylglycine and D-penicillamine and its methyl ester.

In order to contribute to these studies, we have prepared—in solution—Schiff bases of glutamic acid (glu) with salicylaldehyde (sal); 2,3-dihydroxybenzaldehyde (2,3-diOHbenz); 2,4dihydroxybenzaldehyde (2,4-diOHbenz); 2,5-dihydroxybenzal dehyde (2,5-diOHbenz); and o-hydroxynaphthaldehyde (o-OHnaph). Ni(II) complexes of the Schiff bases were synthesized by template reaction using alcohol or ammonia as solvents. They were characterized using elemental analysis, magnetic properties, spectral (IR, UV-vis. and ¹H NMR), and thermal methods (TG, DTG, and DTA). The interaction between the Ni(II) complexes of the Schiff bases and fish melt DNA (FM-DNA) under physiological conditions was investigated by UV and fluorescence spectroscopy.

EXPERIMENTAL

Glutamic acid; salicylaldehyde; 2,3-diOH-; 2,4-diOH-; 2,5diOH-benzaldehyde, and o-hydroxynaphthaldehyde were purchased from Fluka, Aldrich, and Merck. All solvents were of analytical-grade reagents.

Preparation of Sodium Salt of the Schiff Bases

Glutamic acid (2 mmol, 0.294 g) and NaOH (4 mmol, 0.16 g) were suspended in EtOH (10 mL), and H₂O was added drop wise with stirring tell complete dissolution. 2 mmol of the corresponding aldehyde was dissolved in 10 mL of EtOH and was added to the sodium glutamate solution dropwise. The mixture was refluxed with stirring and pubbling of purified N₂ gas for 2 h. The solution turns to yellow color indicating the formation of the Schiff bases. We succeeded to precipitate salicylaldeneglutamic acid Schiff base by reduction of solvent volume followed by acidification using CH₃COOH, but trials to precipitate the other Schiff bases by acidification, evaporation of the solvent, or using solvents mixture were unsuccessful.

Template Synthesis of the Ni(II) Complexes

To the obtained Schiff bases solutions in EtOH/H₂O medium, a solution of NiCl₂.6H₂O (2 mmol, 0.5 g) in 10 mL EtOH was added with stirring and the mixture was refluxed for 1 h. After

Received 12 December 2011; accepted 1 April 2012.

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cooling, the solid complexes were precipitated and washed with EtOH and Et_2O and dried under vacuum. If we added ammonia solution (5 mL 28%) before reflux of the mixture, we obtain another series of Ni(II) complexes in which NH₃ is the coligand instead of H₂O.

Physical Measurements

C, H, and N were estimated using a Heraus CHN-rapid analyzer. The ¹H NMR spectra were traced on Varian-Gemini 200MHz spectrometer in DMSO-d₆ using TMS as internal standard. The IR spectra were recorded (KBr disc) in the $400-4000 \text{ cm}^{-1}$ range on a Bruker Vector 22 spectrometer. The electronic absorption spectra were obtained by nujol mull and 10⁻³M DMF solution in 1 cm quartz cell using UV-1601PC Shimadzu spectrophotometer. Magnetic susceptibility measurements were carried out using the modified Gouy method^[14] on MSB-MK1 balance at room temperature using mercury(II)tetrathiocyanatecobaltate(II) as standard. The effective magnetic moment, μ_{eff} , per metal atom was calculated from the expression $\mu_{\text{eff}} = 2.83\sqrt{\chi \cdot T}$ B.M., where χ is the molar susceptibility corrected using Pascal's constant for the diamagnetism of all atoms in the complexes. TGA, DTG, and DTA were recorded on Shimadzu 60 thermal analyzer under a dynamic flow of nitrogen (30 mL/min) and heating rate 10°C/min from ambient temperature to 750°C. Electrical conductivity measurements were carried out at room temperature on freshly prepared 10^{-3} M DMSO solutions using a WTW conductivity meter (Multiline, Germany) fitted with L100 conductivity cell. Metal content was obtained by EDTA titration using murexide indicator and ammonia buffer.

DNA Interaction

Experiments were carried out in Tris–HCl buffer at pH 7.0. A solution of fish melt DNA gave a ratio of UV absorbance more than 1.8 at 260 and 280 nm, indicating that DNA was sufficiently free from protein.^[15] The stock solution of FM-DNA was prepared by dissolving DNA in 10 mM of the Tris–HCl buffer at pH 7.0. The DNA concentration of the stock solution was determined by UV spectrophotometery—in properly diluted samples—using the molar absorption coefficient $6600 \text{ M}^{-1}.\text{cm}^{-1}$ at 260 nm.^[16] The stock solution was stored at 4°C and used over no more than 4 days.

Absorption titration experiments were performed with fixed concentration of the complexes $(10^{-3}M)$ while gradually increasing the concentration of DNA $(0.5-8\times10^{-4}M)$ at 25°C. While measuring the absorption spectra, an equal amount of DNA was added to both the compound solution and the reference. To compare quantitatively the affinity of the compound

				Ele Fe	ementa ound C	analy alcd (9	/sis %)		
Complex	Color	Mol. Wt.	Melting and Dec. point °C	С	Н	N	М	Ω^{a}	$\mu_{\rm eff}$ B.M.
[Ni(HL ¹)(H ₂ O)].3H ₂ O	Light olive	379.75	>390	31.9	2.8	3.7	15.8	24	Dia
$[Ni(HL^1)(NH_3)]$	Shining brown	324.75	366	37.9 44.6	2.9 3.1	3.7 4.4	15.5 18.2	15	Dia
$[Ni(H_2L^2)(H_2O)_2].4H_2O$	Light brown	431.75	>388	44.3 33.0 33.3	2.7 2.8	4.5 3.1 3.2	13.4 13.6	17	3.1
[Ni(H ₂ L ²)(NH ₃)].1/2H ₂ O	Brown	349.75	>395	41.1 41.2	2.8 3.4 3.4	3.8 4.0	16.3 16.8	14	Dia
$[Ni(H_2L^3)(H_2O)_2].3H_2O$	Light olive	413.75	>380	34.5 34.8	2.8 2.9	3.2 3.4	13.9 14.2	17	3.17
$[Ni(H_2L^3)(NH_3)(H_2O)].3H_2O$	Greenish brown	412.75	>390	34.6 34.9	2.8 2.9	3.5 3.4	13.8 14.2	14	3.23
$[Ni(H_2L^4)(H_2O)_2].4H_2O$	Greenish brown	431.75	>375	33.1 33.4	2.7 2.8	3.1 3.2	13.3 13.6	17	3.25
$[Ni(H_2L^4)(NH_3)(H_2O)].5H_2O$	Deep brown	448.75	>370	32.3 32.2	2.6 2.4	3.2 3.1	12.9 13.0	2	2.97
$[Ni(HL^5)(H_2O)].3H_2O$	Light olive	429.79	>385	44.3 44.7	3.2 3.0	3.4 3.3	13.9 13.7	12	Dia
$[Ni(HL^5)(NH_3)]$	Brown	374.79	>390	51.4 51.2	3.2	3.4 3.7	15.6 15.7	15	1.66

TABLE 1

Analytical data, conductivity, and magnetic moments of the nickel(II) complexes of the glutamic acid Schiff bases

 $^{^{}a}10^{-3}$ M in DMSO, ohm⁻¹.cm².mol⁻¹.

65

bound to DNA by the luminescence titration method, fixed amounts of the complexes (10^{-4} M) were titrated with increasing amounts of DNA at 25°C, over a range of DNA concentrations from 5 to 80 μ M.

RESULTS AND DISCUSSION

Salicylaldeneglutamic Acid Schiff Base

Salicylaldeneglutamic acid was the only isolated Schiff base, which is soluble in ethanol and polar organic solvents. It is stable for about 24 h after which it changed to black sticky material indicating its atmospheric decomposition.

The IR spectrum of the salicylaldeneglutamic acid Schiff base ligand show a broad medium band assigned to the phenolic v(OH) vibration at 3425 cm⁻¹. The azomethine stretching band is observed at 1635 cm⁻¹. The strong absorptions at 1585 and 1457 cm⁻¹ are attributed to the asymmetric and symmetric $v(COO^{-})$ stretch.

Nickel(II) Complexes

The results of microanalyses of the prepared nickel(II) complexes suggest the molecular formulas: $[Ni(HL^{1,5})X].nH_2O$ where $X = H_2O$ and n = 3 or $X = NH_3$ and n = 0; $[Ni(H_2L^{2,3,4})(H_2O)_2].nH_2O$ where n = 4, 3, 4, respectively; $[Ni(H_2L^2)(NH_3)].\frac{1}{2}H_2O$ and $[Ni(H_2L^{3,4})(NH_3)(H_2O)].nH_2O$ where n = 3, 5; and L = Schiff base $(H_3L^1 = glu-sal, H_4L^2 = glu-2,3-diOHbenz, H_4L^3 = glu-2,4-diOHbenz, H_4L^4 = glu-2,5-diOHbenz, H_3L^5 = glu-o-OHnaph).$ The prepared complexes were found to be air stable and they decomposed at temperature greater than 380°C (Table 1) except $[Ni(HL^1)(NH_3)]$, which melts at 334–336°C. They are insoluble in water and most organic solvents but soluble in Lewis bases such as DMF and DMSO. The molar conductance values for 10^{-3} M DMSO solutions of the prepared complexes at $25^{\circ}C$ (2-24 ohm^{-1}cm^2mol^{-1}) indicate the non-electrolytic nature of these complexes.^[17]

Infrared Spectra

Table 2 gives assignments of the most important IR bands for the synthesized nickel(II) complexes.

In order to study the binding mode of the Schiff bases to the nickel(II) ion in the complexes, the IR spectrum of the salicylaldeneglutamic acid Schiff base ligand was compared with the spectra of the nickel(II) complexes. On coordination, due to possible drift of the lone pair density toward the nickel ion, the azomethine (–C=N) bond is expected to absorb at lower frequency in the complexes. The band observed at $\approx 1644-1612$ cm⁻¹ indicates the coordination of the azomethine nitrogen to the nickel(II) ion.^[18] In all the complexes, a new band was shown at 422–560 cm⁻¹ region, which is probably

	TABLE 2	
IR spectral data of the N	(II) complexes of the glutamic acid Schiff bases	
$v(H_2O)$	v(C=N)	

	$v(H_2O)$			v(C=N)						
	and/or			+	v(Ph-C-	$v_{ m sym}$				
Complex	υ(OH)	υ(OH)	v(NH)	$v_{\rm as}$ (COO ⁻)	C=N)	(COO ⁻)	Δv	v(C-O)	υ(M-O)	υ(M-N)
$[Ni(HL^1)(H_2O)].3H_2O$	3381b	—		1634s 1596s	1566s	1334m	262	1298m	558m	457m
$[Ni(HL^1)(NH_3)]$	3446b	—	3302s	1618sh 1578m	1528(s)	1349m	229	1219m	593m	465m
[Ni(H ₂ L ²)(H ₂ O) ₂].4H ₂ O	3402b	3306b	—	1644s 1625s	1569s	1392m	233	1253m	660m	531m
$[Ni(H_2L^2)(NH_3)].\frac{1}{2}H_2O$	3360m	3324m	3281sh	1622sh. 1551m	1507m	1393s	158	1226s	541m	456m
[Ni(H ₂ L ³)(H ₂ O) ₂].3H ₂ O	3348b	3282b	—	1630 ₁₈ 1597	1578s	1342m	255	1218m	676m	560m
[Ni(H ₂ L ³)(NH ₃)(H ₂ O)].3H ₂ O	3411b	3274b	3185b	1625 _] s 1602 []]	1557s	1408m	194	1221m	643m	540m
$[Ni(H_2L^4)(H_2O)_2].4H_2O$	3389b	3242b	—	1625 ₃ 1576	1566s	1346m	230	1226m	676m	560m
[Ni(H ₂ L ⁴)(NH ₃)(H ₂ O)].5H ₂ O	3403b	3314b	3217b	1625 _] s 1561 []]	1550s	1400m	161	1266m	671m	422m
$[Ni(HL^5)(H_2O)].3H_2O$	3395b	3282b	—	1623 ₃ 1585	1550m	1401m	184	1248m	571m	502m
$[Ni(HL^5)(NH_3)]$	3423b	—	3319sh.	$1612 \\ 1600$ ^s	1533s	1396m	204	1242m	550m	438m

Note. sh = sharp; s = strong; b = broad; m = medium.

due to the formation of Ni-N bond.^[19] The complexes exhibit a broad band in the region 3348–3446 cm⁻¹ due to v(O-H) of the coordinated water.^[20] The two absorption bands occurring near 1561–1625 cm^{-1} and 1342–1408 cm^{-1} corresponding to the asymmetric and symmetric stretching vibration bands of the ionic carboxylic group $v(COO^{-})$ which is shifted toward lower frequency compared with the free Schiff bases. The value of $|v_{as}(COO^{-}) - v_{svm}(COO^{-})|$ indicates the monodentate nature of the carboxylate group ($\Delta v = 161-262 \text{ cm}^{-1}$).^[21] The appearance of a new band at 541-676 cm⁻¹ due to Ni-O, further confirms the coordination nature of the carboxylate group.^[22] A medium strong band at 1507–1587 cm⁻¹, always present, may be originated from the vibration of the Ph-C-C-(=N) moiety and typifies complexes derived from salicylaldehyde.^[23-25] Medium strong bands in the range 1218–1298 cm⁻¹ are probably due to the v(Ph-O).

Besides these general features in nickel(II) complexes, H_4L^2 - H_4L^4 Schiff bases complexes show υ (O–H) of the second free OH group as a medium broad band at 3242–3324 cm⁻¹. A strong sharp band appear in the 3185–3319 cm⁻¹ is due to υ (N–H) of the coordinated ammonia.

Magnetic and UV-Vis Spectral Properties

Electronic spectral data and magnetic moments of the nickel(II) complexes are summarized in Table 3.

The recorded visible spectra of the complexes [Ni(HL1) (H_2O)].3H₂O and $[Ni(H_2L^2)(NH_3)]$. $\frac{1}{2}H_2O$ show two bands at 558, 468 and 559, 448 nm (nujol) of ${}^{1}A_{2g} \leftarrow {}^{1}A_{1g}(\upsilon_1)$ and ${}^{1}B_{1g} \leftarrow {}^{1}A_{1g}(\upsilon_2)$ transitions in square planar structure.^[26] In the same time, the square planar complexes $[Ni(HL^1)(NH_3)]$ and $[Ni(HL^5)(NH_3)]$ show only υ_2 transition at 440 and 443 nm (nujol) but in the electronic spectrum of [Ni(HL⁵)(H₂O)].3H₂O, the $d \rightarrow d$ transitions were not observed because the peaks overlapped with the charge transfer bands.^[27] Diamagnetic behavior of these complexes is also in accordance with the proposed square planar structure.^[28] A lack of any absorption bands at wavelength longer than 600 nm indicates a large crystal field splitting and is consistent with the square planar geometry.^[29] Anomalous magnetic moment of the complex $[Ni(HL^5)(NH_3)]$ (1.66 B.M.) may result from either spin-spin coupling^[30] or configurational equilibria.^[31]

Rest of the nickel(II) complexes have magnetic moments in the 2.97–3.25 B.M. range, indicating two unpaired

TABLE 3
Electronic spectra of the nickel(II) complexes of the glutamic acid Schiff bases

		Nujol n	null			DMS	0		
Complex	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	СТ	$d \rightarrow d$	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	СТ	$d \rightarrow d$	$\mu_{\rm eff}$ B.M.
[Ni(HL ¹)(H ₂ O)].3H ₂ O	263	318	368	558	258	326	366		Dia.
		342		468	295	337			
$[Ni(HL^1)(NH_3)]$	260	318	431	440	257	321	406	—	Dia.
		339	358			338			
$[Ni(H_2L^2)(H_2O)_2].4H_2O$	275	334	431	_	251	304		725	3.1
		366	384		256			662	
$[Ni(H_2L^2)(NH_3)].\frac{1}{2}H_2O$	264	318	365	559	294	341	420	_	Dia.
2		342		448					
$[Ni(H_2L^3)(H_2O)_2].3H_2O$	250	320	430	—	257	344	_	728	3.17
		348	362		282			662	
					294				
$Ni(H_2L^3)(NH_3)(H_2O)].3H_2O$	263	318	439	_	260	339	394	724	3.23
		342	369		293			660	
		369						555	
$[Ni(H_2L^4)(H_2O)_2].4H_2O$	275	325	430	—	254	304	411	730	3.25
		350	385		257			666	
			365						
$[Ni(H_2L^4)(NH_3)(H_2O)].5H_2O$	263	317	440	—	255	313	418	735	2.97
		344	357		274	351		670	
								558	
$[Ni(HL^5)(H_2O)].3H_2O$		318	391		259		394		
	275	345	366	_	267	313	414	_	Dia.
$[Ni(HL^5)(NH_3)]$	265	323	423	443	273	313	419	—	1.66
		357	367			332			
						351			

electrons per Ni(II) ion and suggesting an octahedral geometry for the Ni(II) complexes.^[32] The electronic spectra of these complexes show $d \rightarrow d$ bands in the region 735–724 and 670–660 nm. These are assigned to the spin allowed transitions ${}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}(F)$ and ${}^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}(F)$ consistent with their well-defined octahedral configuration. Only the complexes [Ni(H₂L³)(NH₃)(H₂O)₂].3H₂O and [Ni(H₂L⁴)(NH₃)(H₂O)₂].5H₂O show ${}^{3}T_{2g}(P) \leftarrow {}^{3}A_{2g}(F)$ transition of Ni(II) ion in an octahedral geometry at 555 and 558 nm.

¹H NMR Spectra

¹H NMR spectra of the complexes [Ni(HL¹)(NH₃)] and [Ni(HL²)(NH₃)]. $\frac{1}{2}$ H₂O recorded in DMSO-d₆ are shown in Figure 1.

The multisignals at δ 6.47–7.35 and 6.35–6.81 ppm are assigned to aromatic-H protons.^[3] Doublet signals at δ 7.74–7.80 and 7.81–7.85 ppm ($J_{HC=N} = 12$ and 7.6 Hz) are due to H atom of the azomethine group for the two complexes. This suggests the presence of proton transfer equilibrium and the existence of NH tautomer in the studied complexes.^[33-35] Deutration of the DMSO solution of the complexes show the azomethine proton as a singlet at δ 7.77 and 7.78 ppm. The value of J_(NH, H) for pure NH form was found to be ≈ 13 Hz.^[36] The calculations show that, the complex $[Ni(HL^1)(NH_3)]$ exists mainly or even exclusively as NH tautomer. On the other hand, the fraction of NH tautomer for the complex $[Ni(H_2L^2)(NH_3)]$. $\frac{1}{2}H_2O$ is close to 58%. The high field shift of the azomethine proton is assigned to the increase of the shielding effect due to decrease of the electronic cloud density of H atom at α -CH group after coordination with nickel(II) ion.^[37] The signal observed at 8.57-8.63 and 9.25–9.28 ppm (exchangeable with D₂O) may be assigned to NH of the coordinated ammonia or the bonded OH of the phenolic or naphtholic moiety.



FIG. 1. ¹H NMR spectra of some Ni(II) complexes.

Structure of the Nickel(II) Complexes

In the studied complexes, nickel(II) ion is coordinated to the Schiff base as (O–N–O) donor sites through o-OH phenolic or naphtholic group, azomethine nitrogen, and α -carboxylate oxygen in addition to one aqua or ammonia ligand (square planar structure).^[7,38,39] Octahedral nickel(II) complexes have the same coordination sites as the square planar in addition to ε -carboxylate oxygen (ONOO donor) and coordination is completed by two water molecules or one water and one ammonia molecule as a coligand. This structure is similar to that found in the manganese(III) complexes of 2-hydroxy-1naphthyldeneaspartic acid Schiff bases.^[8]

Evidences for the proposed structure are the following:

- In the square planar Ni(II) complexes, the phenolic oxygen is bonded to the Ni(II) ion through protonated OH group, its frequency is overlapped with υ(H₂O) of the hydrated and coordinated water. The IR spectra of the complexes [Ni(HL¹)(NH₃)] and [Ni(HL⁵)(NH₃)] show υ(OH) of the coordinated hydroxyl group as broad band at 3446 and 3423 cm⁻¹. The γ-carboxyl group of the glutamic acid Schiff bases does not share in coordination process may be due to steric hindrance. In the same time, the υ(C=O) band (1720 cm⁻¹), which is characteristic to the uncoordinated carboxylic group is not observed in the IR spectra of the complexes, which prove the ionization of this group.
- The pK_a values for the carboxylic groups of the free glutamic acid are 2.19 (α -COOH) and 4.25 (γ -COOH),^[40] and of the free salicylaldehyde is 8.2 in water^[41] and 10.17 in dioxan-water medium.^[42] The pK_a values of the salicylglycine are 3.44 for the carboxylic acid group and 8.24 for the phenolic group.^[43] Recently, Schiff bases of sal-Cl-gly, sal-Cl-ala, sal-Br-gly, and sal-Br-ala were synthesized and the protonation constants of the carboxylate anion are 9.6–10.74 and that of the phenolate anion are 1.86–2.22.^[44] These figures show that the carboxylic groups of the salcylidene- and naphthyldeneglutamic



FIG. 2. TG, DTG, and DTA analysis of [Ni(H₂L⁵)(NH₃)].

acid Schiff bases are ionized before the phenolic and naphtholic OH. This result indicates that $H_3L^1-H_3L^5$ Schiff bases are dibasic tridentate in square planar stereochemistry or tetradentate in octahedral geometry (Scheme 1).

R = H or o - OH $X = H_2O \text{ or } NH_3$ Square planar structure $M = \frac{1}{R} + \frac{1}{R} +$

R = 0-OH, m-OH or p-OH

X=H₂O or NH₃

Octahedral structure

SCH. 1. Ni(II) complexes of the glutamic acid Schiff bases.

Thermal Analysis

TG/DTG and DTA curves of the nickel(II) complexes are shown in Figure 2 (as an example). The phenomenological aspects are illustrated in Tables 4 and 5.

The dehydration process for all complexes is very similar, they lose crystallization water in a single step, which is the first decomposition stage. It takes place in the temperature range $32-192^{\circ}$ C with DTG peaks at 80, 81, 57, 85, 73, 83, 74, and 78°C, giving endothermic DTA peaks in the 28–210°C range with maxima at 80, 88, 59, 91, 81, 89, 82, and 84°C, respectively. The complexes [Ni(HL¹(NH₃)] and [Ni(HL⁵)(NH₃)] have no hydrated water.

The anhydrous nickel(II) complexes decompose in the second decomposition stage mainly in the coordination sphere. All the complexes lose the coligand $(H_2O \text{ or } NH_3)$ associated with Schiff base dissociation. The complex $[NiL^{1}(H_{2}O)].3H_{2}O$ gives H₂O associated with the fragment C₂H₅COOH at 366°C with recorded mass loss 25.12% (calcd. 24.15%) accompanied with exothermic DTA peak at 366°C. Water or ammonia along with the species $C_3H_8(COOH)_2$ are evolved in the second decomposition step for the complexes $[Ni(HL^1)(NH_3)]$, $[Ni(H_2L^2)(H_2O)_2].4H_2O, [Ni(H_2L^3)(H_2O)_2].3H_2O, [Ni(H_2L^4)]$ $(H_2O)_2$].4H₂O, [Ni(HL⁵)(H₂O)].3H₂O, and [Ni(HL⁵)(NH₃)], with DTG peaks at 333, 377, 390, 361, 380, and 362°C, respectively. Weight loss observed is (Found/Anal. Calcd. [%]) 45.33/46.49, 39.2/39.37, 41.45/41.1, 39.4/39.4, 35.9/35.26, and 41.86/41.77 accompanied with exothermic DTA peaks at 334, 367, 398, 350, 374, and 351°C, respectively. [Ni(HL¹)(NH₃)] is the only complex which has a melting point $(336^{\circ}C)$ that is confirmed by sharp endothermic DTA peak at 334°C. In a different manner for the second decomposition stage, $[Ni(H_2L^2)$ (NH_3)]. $\frac{1}{2}H_2O$ loses NH₃ and CO₂, while both $[Ni(H_2L^3)]$ $(NH_3)(H_2O)$].3H₂O and $[Ni(H_2L^4)(NH_3)(H_2O)]$.5H₂O lose NH₃, H₂O, and CH₃COOH with reduced masses of 17.15%, 22.85%, and 21.1% (calcd. 17.44%, 23.02%, and 21.16%) at 353, 327, and 391°C associated with exothermic DTA maxima at 355, 329, and 359°C, respectively. Final decomposition includes dissociation of the remaining part of the Schiff bases with the formation of NiO residue except [Ni(HL¹)(H₂O)].3H₂O, which gives NiCO₃ as a final product.

To speculate the probable decomposition mechanism of the complexes $[Ni(H_2L^2)(H_2O)_2].4H_2O$ and $[Ni(H_2L^2)(NH_3)].\frac{1}{2}H_2O$, IR spectra of heated samples of the complexes are recorded at 200, 430, 510, 600°C and 170, 350, 450, 530°C, (an example is given in Figure 3).

The IR spectra of the heated $[NiL^2(H_2O)_2].4H_2O$ and $Ni(H_2L^2)(NH_3)]_{\frac{1}{2}}H_2O$ at 200 and 170°C, respectively, show no difference when compared with that obtained at room temperature, indicating dehydration. [44] Heated samples at 430 and 350°C show IR spectra as a sharp medium band at 2358 and 2362 cm⁻¹, respectively, which may be ascribed to the formation of $(-C \equiv N)$ group.^[21] Also, the vibrations due to the carboxylate group, v(NH) of the ammonia which act as coligand and v(C=N) were disappeared. New medium broad bands at 3434, 3435 cm⁻¹; medium to weak bands at 2930, 2923 cm⁻¹; 2865, 2872 cm⁻¹; and 1645, 1643 cm⁻¹ may be assigned to v(OH), $v(CH_2)$, and $\Delta(OH)$, respectively, of aqua-hydroxo species.^[45] NiO is the final product as shown by the strong v(Ni-O) band at 417 and 420 cm^{-1} in the IR spectra of the complexes heated at 600 and 530°C. The mechanism of thermal decomposition of $[Ni(H_2L^2)(H_2O)_2].4H_2O$ is shown as follows:





FIG. 3. IR spectra of $[Ni(H_2L^2)(NH_3)]$. $\frac{1}{2}H_2O$ at different temperatures.

Kinetic Parameters

All the well-defined stages were selected for the study of the kinetics of the decomposition of the nickel(II) complexes. The order of the decomposition process (n), the activation energy ΔE_a and the pre-exponential factor (Z) were calculated using the Coats-Redfern equation.^[46] Thermodynamic parameters of the decomposition process ΔG° , ΔH° , and ΔS° were also evaluated. The kinetic parameters are listed in Table 6.

The activation energy ΔE_a in the first decomposition step are in the 45–64 kJ.mol⁻¹ range and in the 47–192 kJ.mol⁻¹ range for the second decomposition step. The respective values of the pre-exponential factor (Z) vary from 1.5×10^5 to $5.2 \times 10^8 \, s^{-1}$. The corresponding values of the entropy of activation ΔS° are in the range –85 to –167 J.mol⁻¹.K⁻¹. The negative values of the entropy of activation indicate that the activated complexes have a more ordered structure than the reactants.^[47]

DNA Interaction

Assuming that DNA forms a 1:1 systems with Ni(II)complexes, the binding constant of the formed complexes (K_b)

				I ULU ILLUNULUUUUUUUUUUUUUUUUUUUUUUUUUUU	voluptiones of the glutaline and	a Julii Dasus	
	Temn	DTG	Ma	ss loss%			Residue Found
Complex	range °C	temp. °C	Found	Anal. Calcd.	Process	Expected products	(Anal. Calcd.)%
[Ni(HL ¹)	35-134	80	15.0	14.2	Dehydration	$3 H_2 O$	NiCO ₃
(H_2O)].3 H_2O	329–390	366	25.12	24.15	Coordination sphere	$H_2O + C_2H_5COOH$	31.3 (31.2)
		386			ı		
[Ni(HL ¹)(NH ₃)]	400-550	483	28.9	29.75	Final decomposition	0.45 L	
	248-397	333	45.33	46.49	Coordination sphere	$NH_3 + C_3H_8(COOH)_2$	NiO
	400 - 680	562	31.7	30.9	Final decomposition	0.4 L	22.4
$[Ni(H_2L^2)]$	30 - 187	81	15.6	16.6	Dehydration	$4 H_2 O$	NiO
$(H_2O)_2$].4H ₂ O	200-576	377	39.2	39.37	Coordination sphere	$2 H_2 O + C_3 H_8 (COOH)_2$	16.7 (17.3)
		485	28.02	26.6	Ligand decomposition	0.43 L	
$[Ni(H_2L^2)]$	34 - 142	57	2.2	2.6	Dehydration	$\frac{1}{2}$ H ₂ O	NiO
$(NH_3)].\frac{1}{2}H_2O$	294-610	353	17.15	17.44	Coordination sphere	$ { m NH}_3+ m CO_2$	20.0 (21.2)
1		386	60.22	58.79	Ligand	0.77 L	
		582			decomposition		
$[Ni(H_2L^3)]$	36-185	85	12.8	13.1	Dehydration	$3 H_2 O$	NiO
$(H_2O)_2$].3 H_2O	200-600	390	41.45	41.1	Coordination sphere	$2H_2O +$	19.5 (18.1)
		478	26.07	27.75	Ligand decomposition	$C_3H_8(COOH)_2$	
		531			Solid stat reaction	0.43 L	
$[Ni(H_2L^3)(NH_3)$	32 - 160	73	12.8	13.1	Dehydration	$3 H_2 O$	NiO
(H_2O)].3 H_2O	230–350	327	22.85	23.02	Coordination sphere	$NH_3 + H_2O + CH_3COOH$	20.2 (18.1)
	360-530	400	44.57	45.3	Ligand decomposition	0.7 L	
		447			Final decomposition		
$[Ni(H_2L^4)$	40-170	83	15.6	16.7	Dehydration	$4 H_2 O$	NiO
$(H_2O)_2].4H_2O$	240–525	361	39.4	39.4	Coordination sphere	$2 H_2 O + C_3 H_8 (COOH)_2$	19.1 (17.25)
		483	25.8	26.59	Final decomposition	0.43 L	
$[Ni(H_2L^4)(NH_3)]$	33-192	74	19.9	20.05	Dehydration	5 H ₂ O	NiO
(H_2O)].5 H_2O	230-440	391	21.1	21.16	Coordination sphere	$NH_3 + H_2O + CH_3COOH$	15.8 (16.64)
	450–661	550	43.3	43.44	Ligand decomposition	0.73 L	
[Ni(HL ⁵)]	38-150	78	12.52	12.53	Dehydration	$3 H_2 O$	NiO
(H_2O)].3 H_2O	280–550	380	35.9	35.26	Coordination sphere	$H_2O + C_3H_8(COOH)_2$	18.3 (17.4)
		485	33.84	34.71	Final decomposition	0.49 L	
[Ni(HL ⁵)(NH ₃)]	277–380	362	40.16	40.29	Coordination sphere	$NH_3 + C_3H_8(COOH)_2$	NiO
	420–560	444	41.86	41.77	Final decomposition	0.52 L	18.1(19.91)
	570-692	650			Solid stat reaction		

TABLE 4 TGA and DTG of the nickel(II) complexes of the glutamic acid Schiff bases

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Complex	Temp. range °C	DTA temp. °C	$\Delta H (J/g)$	Process
$\frac{1}{[Ni(HL^1)(H_2O)].3H_2O}$	28-221	80 endo.	722	Dehydration
	262-400	366 exo.	-6180	Coordination sphere
		383		Ligand decomposition
	410-541	480 exo.		Final decomposition
$[Ni(HL^1)(NH_3)]$	271-394	334 endo.		Melting
	394-700	559 exo.	-5870	Coordination sphere
$[Ni(H_2L^2)(H_2O)_2].4H_2O$	30-193	88 endo.	799	Dehydration
	225-576	367		Coordination sphere
		486 exo.	-5840	Final decomposition
		537		Solid state reaction.
$[Ni(H_2L^2)(NH_3)].\frac{1}{2}H_2O$	28-101	59 endo.	59	Dehydration
	206-632	355		Coordination sphere
		396 exo.	-9300	Ligand decomposition
		577		Final decomposition
$[Ni(H_2L^3)(H_2O)_2].3H_2O$	36-182	91 endo.	676	Dehydration
	284-525	398		Coordination sphere
		450 exo.	-6060	Final decomposition
		536		Solid state reaction
$[Ni(H_2L^3)(NH_3)(H_2O)].3H_2O$	32-174	81 endo.	691	Dehydration
	205-340	329 exo.		Coordination sphere
		404 exo.		Ligand decomposition
	350-520	447	-10510	Final decomposition
$[Ni(H_2L^4)(H_2O)_2].4H_2O$	33-210	89 endo.	819	Dehydration
	232-468	350 exo.	-7960	Coordination sphere
		491		Final decomposition
[Ni(H ₂ L ⁴)(NH ₃)(H ₂ O)].5H ₂ O	27-198	82 endo.	916	Dehydration
	328-400	359 exo.	-65	Coordination sphere
	420-600	553 exo	-11	Final decomposition
$[Ni(HL^5)(H_2O)].3H_2O$	33-182	84 endo	517	Dehydration
	231-550	374 exo.	-7280	Coordination sphere
		485		Final decomposition
$[Ni(HL^5)(NH_3)]$	296-380	351 exo.	-3880	Coordination sphere
	420-600	440 exo.	-2000	Ligand decomposition
	617-677	652 exo.	-246	Solid state reaction

 TABLE 5

 DTA of the nickel(II) complexes of the glutamic acid Schiff bases complexes

is given by Benesi-Hildebrand plot^[48]:

$$\frac{[\text{Ni} - \text{complex}]_0}{\Delta A} = \frac{1}{\Delta \varepsilon} + \frac{1}{\text{K[DNA]}_0 \Delta \varepsilon}$$

Where ΔA is the difference between the absorbance of Ni(II)complex in the presence and absence of DNA and $\Delta \varepsilon$ is the difference between the molar absorption coefficients of Ni(II)complex and Ni(II)-complex-DNA system. [Ni(II)-complex]₀ and [DNA]₀ are the initial concentration of the Ni(II)-complex and DNA. Linear relationship of [Ni(II)-complex]/ ΔA versus 1/[DNA] confirms the formation of a 1:1 Ni(II)-complexes-DNA system. From its intercept and slope values, K_b is evaluated at room temperature (25°C). The changes of emission intensity in emission titrations ensured the availability of the association constants (K) of the complexes with DNA from the analysis of the relationship between the fluorescence intensity and [DNA] by Benesi–Hildebrand plot.^[48] The association constants of the formed complexes (K) are given by

$$\frac{I_{F0}}{I_F - I_{F0}} = \alpha + \frac{\alpha}{K \lceil DNA \rceil 0}, \quad \alpha = \frac{1}{I_{FL} - I_{F0}}$$

Where $[DNA]_0$ represents the analytical concentration of DNA, I_{F0} and I_F are the fluorescence intensities in the absence and presence of DNA, I_{FL} is the limiting intensity of fluorescence

Complex		Order n	Ts K ^o	$^{b}\Delta E^{a}$	°Z	$^{d}\Delta S^{^{\circ}}$	$^{b}\Delta H^{^{\circ}}$	${}^{b}\Delta G^{^{\circ}}$
[Ni(HL ¹)(H ₂ O)].3H ₂ O	Ι	2	354	57	29	-103	54	37
	Π	0.5	657	128	5.2	-85	123	56
$[Ni(HL^1)(NH_3)]$	Π	0	607	153	62	-102	148	62
$[Ni(H_2L^2)(H_2O)_2].4H_2O$	Ι	2	356	61	490	-118	58	42
	Π	2	648	53	2.7	-90	48	58
$[Ni(H_2L^2)(NH_3)].\frac{1}{2}H_2O$	Π	2	625	163	660	-121	158	75
$[Ni(H_2L^3)(H_2O)_2]^{2}.3H_2O$	Ι	2	357	61	390	-120	58	43
	Π	2	661	87	56x	-103	82	68
$[Ni(H_2L^3)(NH_3)(H_2O)].3H_2O$	Ι	0.5	348	45	150	-167	42	58
	Π	0	600	47	39	-106	43	63
$[Ni(H_2L^4)(H_2O)_2].4H_2O$	Ι	2	356	59	240	-124	56	44
	Π	2	636	91	1.9	-93	86	59
[Ni(H ₂ L ⁴)(NH ₃)(H ₂ O)].5H ₂ O	Ι	2	347	58	230	-123	55	56
$[Ni(HL^5)(H_2O)].3H_2O$	Ι	2	350	64	26	-104	66	37
	Π	2	653	91	2.3	-91	86	60
$[Ni(HL^5)(NH_3)]$	Π	2	635	392	65	-102	387	65

 TABLE 6

 Kinetic parameters for the decomposition steps of the nickel(II) complexes of the glutamic acid Schiff-bases

^cvalues x 10^8 ; s⁻¹.

and α is $1/(I_{FL} - I_{F0})$. A plot of $I_{F0}/(I_F - I_{F0})$ vs. $1/[DNA]_0$ should give a straight line with a good linear relationship.

Electronic Absorption Titration

The absorption spectra of the complexes of Ni(II)-glut. Schiff bases in presence of FM-DNA (at a constant concentration of the complexes) are given in Figure 4 and Table 7.

The potential FM-DNA binding ability of the complexes was studied by following the intensity changes of the intraligand $\pi - \pi^*$ transition bands in the UV spectra.^[49] In presence of DNA, the absorption bands of the complexes at about 223–270 nm exhibited hyperchromism of about 3–84% and blue shift of about

3–9 nm. Therefore, the observed hyperchromism reflect strong structural damage, which is probably due to strong binding of the complexes to the DNA base moieties through covalent-bond formation.^[50] The intrinsic binding constants K_b of the complexes were in the 1.1×10^4 – 6.4×10^4 M⁻¹ range. The obtained values indicate that the nickel(II) complexes are moderately bind to FM-DNA with almost the same affinity. However, these values are smaller than those of classical intercalators whose K_b values are in order of 10^7 M⁻¹.^[51] Therefore, it is likely that the proposed covalent binding of the complexes is more feasible although electrostatic interactions can not be ruled out.

TABLE	7
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Binding constants (K M⁻¹) of the interaction between the Ni(II) complexes of the glutamic acid Schiff bases and FM-DNA

		UV.			Fluorescence	
Complex	$K_b M^{-1}$	Hyper.%	Δ/λ	K M ⁻¹	Hyper. %	Δ/λ
$[Ni(HL^{1})(H_{2}O)].3H_{2}O$	2.0×10^{4}	10		3.5×10^{4}	71	_
$[Ni(HL^1)(NH_3)]$	5.9×10^{4}	69	-3	3.2×10^{4}	63	
$[Ni(H_2L^2)(H_2O)_2].4H_2O$	1.1×10^{4}	9	-4	1.6×10^{4}	47	-15
$[Ni(H_2L^2)(NH_3)].1/2H_2O$	5.2×10^{4}	3		3.3×10^{4}	58	
$[Ni(H_2L^3)(H_2O)_2].3H_2O$	1.5×10^{4}	13	_	7.4×10^{4}	76	
$[Ni(H_2L^3)(NH_3)(H_2O)].3H_2O$	7.2×10^{4}	55	_	3.1×10^{4}	55	-8
$[Ni(H_2L^4)(H_2O)_2].4H_2O$	6.2×10^{4}	68	-5	9.7×10^{4}	76	
[Ni(H ₂ L ⁴)(NH ₃)(H ₂ O)].5H ₂ O	4.2×10^{4}	84	-9	2.3×10^{4}	44	
$[Ni(HL^5)(H_2O)].3H_2O$	6.4×10^{4}	43	_	6.1×10^{4}	65	
$[Ni(HL^5)(NH_3)]$	3.2×10^4	60	-5	2.8×10^4	57	—

^bkJ/mol.

^dkJ/mol.K.



FIG. 4. Electronic spectra of 10^{-3} M [Ni(HL¹(NH₃)] in the presence of increasing amounts of FM-DNA, $0-8 \times 10^{-5}$ M (color figure available online).



FIG. 5. The emission enhancement spectra of 10^{-4} M [Ni(HL¹(NH₃)] in the presence of 0–80 μ M FM-DNA (color figure available online).

Fluorescence Titration Studies

The nickel(II) complexes under study can emit fluorescence in Tris-HCl buffer at ambient temperature with maxima appearing at about 425–500 nm. As shown in Figure 5, the fluorescence intensities of the complexes are increased steadily with increasing concentration of FM-DNA, which agrees with those observed for other intercalators^[52] and pronouncing their interaction with FM-DNA. This implies that the complexes can insert between DNA base pairs deeply and that they can bind to DNA. The binding of the complexes to DNA leads to a marked increase in emission intensity which is also observed with complexes containing ligands bearing NH and OH groups.^[53,54] The association constant (K) evaluated using Bensi-Hildebrand plot is 1.6–7.4 × 10⁴ M⁻¹.

CONCLUSION

Schiff bases of glutamic acid with salicylaldehyde, 2,3-; and 2,5-dihydroxybenzaldehyde; and o-hydroxynaphthaldehyde and their nickel(II) complexes have been synthesized by template method in ethanol or ammonia media. Magnetic and spectral properties show that three types of the complexes were obtained. Diamagnetic square planar, octahedral with $\mu = 2.97 - 3.25$ B.M. and a complex with $\mu =$ 1.66 B.M.-indicating spin-spin interaction or configurational equilibrium-were obtained. The complexes decompose starting by evolution of crystallization water followed by decomposition of the coordination sphere. Interactions of the complexes with FM-DNA show hyperchromism and blue shift of their UV and florescence spectra, which reflect structural damage probably due to binding of the complexes to DNA. The intrinsic binding constants K_b of the complexes were in the 1.1×10^4 – 6.4×10^4 M⁻¹ range, which are smaller than those of classical intercalators.

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