# Acid-Catalyzed Aquation of Ni(II)-Hydrazone Complexes: Kinetics and Solvent Effect

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> ABSTRACT: Complexes of the type  $[Ni(L)(H_2O)]Cl_2 \cdot nH_2O$ , where L = 2-pyridyl-3isatinbishydrazone ligands, have been synthesized and characterized on the bases of elemental analysis, molar conductance, IR, electronic spectra, and thermal analysis (TGA and DTA). Acidcatalyzed aquation of the Ni(II) isatin-bishydrazone complexes was followed spectrophotometrically in various water-methanol and water-acetone mixtures at temperature 298 K. Kinetic behavior of the acid aquation is a linear rate law, indicating that the acid-catalyzed aquation of these complexes in water-methanol and water-acetone mixtures follows a rate law with  $k_{obs} = k_2[H^+]$ . The effect of the mole fraction of the ganic solvent, i.e., methanol and acetone, on the acid aquation has been analyzed; the decrease in the rate constant values with increasing of the methanol or acetone ratios is attributable to the effect of the co-organic solvent on the initial states of the acid aquation by the destabilization of the H<sup>+</sup> ion. © 2014 Wiley Periodicals, Inc. Int J Chem Kinet 46: 451–461, 2014

## INTRODUCTION

The preparation of a new ligand was perhaps the most important step in the development of metal complexes, which exhibit unique properties and novel reactivity. Schiff bases are an important class of ligands with wide applications in biology, clinics, analysis, and industry in addition to their important roles in catalysis and organic synthesis [1]. A considerable number of Schiff base complexes have potential biological interest, being used as biological models in understanding of the structure of biomolecules and biological process [2]. Schiff base ligands containing various donor atoms (such as N, O, S) show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities [3]. In the past few years, a wide range of metal compounds, which contain the isatin moiety, have received a lot of attention in the fields of inorganic chemistry, biochemistry, and environmental chemistry. Isatin, an endogenous indole, and its derivatives have exhibited a wide range of biological activities [4–8]. A significant increasing interest in the designing of metal compounds

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Scheme 1 Schematic diagram of the isatin-bishydrazone ligands and their Ni(II) complexes.

as drugs and diagnostic agents is directly observed in the area of scientific inquiry appropriately termed medicinal inorganic chemistry [9]. Metal complexes with Schiff bases of isatin derivatives exhibited remarkable biological activity [10-12]. Although much attention has been directed to study the metal complexes of the Schiff base ligands derived from isatin [13,14], no investigations have appeared in the literature to describe the metal complexes of the Schiff base derived from isatin monohydrazone and 2-pyridyl. Thus, our interest is in the synthesis and structural characterization of new Schiff bases [15] We synthesized and characterized new isatin-bishydrazone compounds derived from isatin monohydrazone and 2-pyridyl, which show notable biological activity, also reported in other work [16,17], and new Ni(II) complexes with the previously synthesized bioactive isatin-bishydrazone ligands, with studies on their biological activity.

The rate coefficient for the reaction between organic and inorganic compounds with hydrogen ions in aqueous solutions is sensitive to the nature and molar fraction of organic cosolvent. The rate constants in binary aqueous mixtures depend on the composition of the solvent [18,19]. Less information is available in the literature on the acid-catalyzed aquation of Ni(II) complexes in various reaction media and their mechanistic pathways.

Thus, in view of the significant importance of these complexes, we are interested in the investigation and report the acid hydrolysis of these complexes, in addition investigate the effects of methanol and acetone as organic cosolvents on the kinetics of the acid hydrolysis of these complexes to gain more information about the acid hydrolysis of these new bioactive complexes. Methanol and acetone have been chosen as a cosolvent due to the availability of previously measured chemical potentials, which aided in the interpretation of the rate constant data.

The structures of the prepared Ni(II) complexes in this investigation are shown in Scheme 1.

## **EXPERIMENTAL**

#### **Chemicals and Apparatus**

*Chemicals.* All chemicals were used as received without further purification. Isatin, 2-acetyl pyridine, 2-benzoyl pyridine, and pyridine-2-carboxaldhyde were obtained from Sigma-Aldrich. Hydrazine hydrate and hydrated nickel chloride (NiCl<sub>2</sub>·6H<sub>2</sub>O) were obtained from BDH. All other reagents and solvents (methanol, ethanol, and DMF) were purchased from commercial sources and were of analytical grade. Hydrochloric acid was used as received from Merck (37 wt% in water (99.99%)), and water used was doubly distilled. The stock solutions of HCl and NaCl were freshly prepared by dissolving the calculated amounts of AnalaR samples in redistilled water.

Apparatus and Methods. IR spectra of the current Isatin-bishydrazone ligands and their corresponding complexes were monitored using a Shimadzu FTIR model 8101 (within the region of 4000–400  $cm^{-1}$  using dry KBr disks). Conductivity measurements were carried out using a Jenway conductivity meter model 4320 at 298 K, which was controlled by an ultrathermostat (Crioterm model 190) to control the temperature at  $25 \pm 0.1$  °C). The elemental analyzer Perkin–Elmer model 240c was used for microanalysis. The thermal gravimetric analysis (TGA) of the recent Ni(II) complexes was performed by a Shimadzu thermal analyzer model 50H using air as the carrier gas. The complexes were heated at the rate of 10°C per min from 25 to 600°C. The UV-vis spectra and the kinetic measurements of the current complexes were performed using 10-mm matched silica cells in the thermostated cell holder of a Jasco UV-vis model V-530 spectrophotometer. The thermostated cell holder was supplied with an ultrathermostate water circulator (Crioterm model 190) to control the temperature at  $25 \pm 0.1$  °C and other temperatures.

# Synthesis of the Isatin-Bishydrazone Ligands and Their Corresponding Ni(II) Complexes

*Synthesis of the Isatin-Bishydrazone Ligands.* Isatin-bishydrazone ligands, namely [(pyridine-2carboxaldhyde)-3-isatin]-bishydrazone (cpish), [(2acetyl pyridine)-3-isatin]-bishydrazone (apish), and [(2-benzoyl pyridine)-3-isatin]-bishydrazone (bpish), were prepared in two steps: The first step was the synthesis of isatin-monohydrazone, followed by condensation with the 2-pyridyl, giving the isatinbishydrazone ligands.

<b>Table I</b> Analytic	cal and Physical Data of Ligands and T	heir Compley	Kes									
						Elen Found	iental An (Calculat	alysis ed) (%)		$\mu_{ m V}$ ( $\Omega^{-1}$	l cm <sup>2</sup> m	$\mathbf{bl}^{-1}$
	Empirical Formula (Formula Weight)	Color	Melting Point (°C)	Yield (%)	C	Н	z	C	M	Methanol	DMF	Ethanol
cpish	$C_{14}H_{10}N_4O$	Red	245	89	67.19	4.03	22.39	I	I	I	I	I
	(250.255)				(67.20)	(4.33)	(22.30)					
Ni-cpish complex	[Ni (cpish) H <sub>2</sub> O]Cl <sub>2</sub> ·2H <sub>2</sub> O	Dark brown	>300	65	38.84	3.49	12.94	16.38	13.56	170	140	85
	(433.89)				(38.75)	(3.72)	(12.91)	(16.34)	(13.53)			
apish	$C_{15}H_{12}N_4O$	Red	250	85	68.17	4.58	21.20	I	I	I	Ι	I
	(264.28)				(68.50)	(4.25)	(20.98)					
Ni-cpish complex	[Ni (apish)H <sub>2</sub> O]Cl <sub>2</sub> ·2H <sub>2</sub> O	Dark brown	>300	09	40.31	3.83	12.54	15.87	13.13	166	137	82
	(447.93)				(40.22)	(4.05)	(12.51)	(15.83)	(13.10)			
bpish	$\mathbf{C}_{20}\mathbf{H}_{14}\mathbf{N}_{4}\mathbf{O}$	Red	265	85	73.61	4.32	17.17	I	I	I	I	I
	(326.35)				(73.55)	(4.28)	(17.05)					
Ni-cpish complex	$[Ni(bpish) H_2 O]Cl_2 \cdot 2H_2 O$	Dark brown	>300	70	47.29	3.57	11.03	13.96	11.55	160	133	80
	(509.99)				(47.10)	(3.95)	(10.99)	(13.90)	(11.51)			

										Electronic Spectra			
No.	Compound	ν (OH) <sup>1</sup>	ν (N–H) <sup>2</sup>	ν (C=O) <sup>3</sup>	$\nu$ (HC=N) <sup>4</sup>	ν (C=N) <sup>5</sup>	ν (M–O)	ν (M–N)	$\lambda_{max}$ (nm)	$\varepsilon_{\rm max}$ (dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )	Assignment		
1	Cpish	3421.2	3276.5	1721.7	1613.7	1460.3			237	1744.05	$\pi$ – $\pi$ $^{*}$		
									324	865.49	n $-\pi$ *		
2	Ni-cpish	3430.8	3287.1	1685.0	1611.7	1409.0	656.8	510.2	284	696.97	Intraligand band		
	-								399	636.84	LMCT band		
									627	320.12	d–d band		
									676	293.02	d–d band		
3	Apish	3393.2	3180.0	1721.7	1618.5	1458.4			254	538.30	$\pi$ – $\pi$ $^{*}$		
									274	580.97	$\pi$ – $\pi$ $^{*}$		
									325	339.05	n $-\pi$ *		
4	Ni-apish	3357.5	3159.8	1672.5	1592.4	1463.2	637.6	504.4	244	1578.13	Intraligand band		
									320	886.64	LMCT band		
									625	723.22	d–d band		
									680	256.57	d–d band		
5	Bpish	3424.0	3181.0	1721.7	1607.9	1452.6			252	1096.47	$\pi$ – $\pi$ $^{*}$		
									271	882.56	$\pi$ – $\pi$ $^{*}$		
									327	653.87	n $-\pi$ *		
6	Ni-bpish	3359.4	3160.7	1671.5	1594.4	1463.2	636.6	503.5	244	1828.62	Intraligand band		
	_								352	817.06	LMCT band		
									399	722.84	LMCT band		
									636	268.80	d–d band		
									682	295.95	d–d band		

**Table II** Infrared Absorption Frequencies (cm<sup>-1</sup>) and Electronic Spectra of the Investigated Isatin-Hydrazone Ligands and Their Metal Complexes

<sup>1</sup>Vibrations of the water molecules, <sup>2</sup>Vibrations of the Indol ring (N–H), <sup>3</sup>Vibrations of the lactonyl group (C=O), <sup>4</sup>Vibrations of the azomethine group (C=N), <sup>5</sup>Vibrations of group from the  $\beta$ -hydrazone of isatin (C=N), LMCT = ligand metal charge transfer.

*Synthesis of Isatin-Monohydrazone.* Isatin (1.47 g, 10 mmol) was dissolved in methanol (40 mL) and was added to a solution of hydrazine hydrate (0.05 g, 10 mmol) dissolved in hot methanol (5 mL). The resulting mixture was refluxed for 3 h in a water bath. On cooling, the yellow compound that formed was filtered, washed with cold methanol, dried, and recrystallized from methanol [20].

*Synthesis of Isatin-Bishydrazone Ligands.* 1.0 mmol of 2-pyridyl (2-acetyl pyridine or 2-benzoyl pyridine or pyridine-2-carboxaldhyde) was added dropwise to a hot methanolic solution of isatin-monohydrazone (1.0 mmol), the resulting mixture was refluxed for 1 h with constant stirring, and then two to three drops of glacial acetic acid was added with continued refluxing for 4 h under constant magnetic stirring. On cooling, the formed ligand was filtered, washed with cold methanol, dried, and finally recrystallized from methanol [21].

Synthesis of Ni(II) Complexes. A solution of the metal salt in a minimum amount of water (NiCl<sub>2</sub>· $6H_2O$ ; 1.0 mmol) was added dropwise to a hot methanolic solution of the ligand (cpish or apish or bpish; 1.0 mmol). The resulting mixture was refluxed at 70°C for 10 h under constant stirring. By evaporation overnight, the re-

sulting solid product was filtered, washed with a watermethanol solvent, dried, and finally recrystallized from the water-methanol mixed solvent. The yield and melting point of each product were determined [16].

## Acid-Catalyzed Aquation of Ni(II) Complexes

Kinetics of the acid-catalyzed aquation of the Ni(II)isatin-bishydrazone complexes was measured by following the time dependence of absorbance using 10mm silica cells in a thermostated cell compartment of a Jasco's model V-530 spectrophotometer. The temperature  $(25 \pm 0.1^{\circ}C)$  was adjusted by a Crioterm 190 ultrathermostate. The required volume of the isothermal reacting stock solutions was taken by a syringe and mixed in 10-mm cells in the thermostated cell jacket compartment. Chemical reactions were monitored in solutions held at constant ionic strength using appropriate amounts of sodium chloride over at least three half-live times. The reaction was carried out under pseudo-first-order conditions with respect to a substrate by mixing multifold greater concentrations of HCl than that of the compound. The substances were added to the cell in the following order: (1) substrate, (2) methanol fraction, (3) salt, (4) water, and finally HCl; the total volume of the cell was 3 mL. Before

adding HCl into the cell, the cell was allowed to take the required temperature of the jacket compartment of the spectrophotometer. The run started simultaneously after the addition of HCl. It was confirmed that there was no interference from other reagents at the selected wavelength absorption maxima for the investigated compounds.

# **RESULTS AND DISCUSSION**

## **Identification of the Prepared Compounds**

*Microanalysis and Molar Conductance Measurements.* The results of the microanalysis of the prepared isatin-bishydrazone ligands and their Ni(II) complexes in addition to the molar conductance measurements (cf. Table I) suggested that the subject ligands act as neutral tridentate and form complexes in the 1:1 molar ratio (metal to ligand), with 1:2 electrolytic nature of all the complexes [22,23].

#### **Spectroscopic Studies**

*IR Spectra and Mode of Bonding.* The significant infrared bands of the subject ligands and their metal complexes are given in Table II. The observed bands may be classified into those originating from the ligands and those arising from the bonds formed between metal ions and the coordinating sites. The IR spectra of the isatin-bishydrazone ligands exhibited character-

istic bands due to (–NH) and lactonyl carbon  $\nu$ (C=O) at  $\approx$ 3180–3200 and  $\approx$ 1722 cm<sup>-1</sup> [24], respectively. In addition, the strong band at  $\approx 1460 \text{ cm}^{-1}$  and a characteristic high intensity band at  $\approx 1621 \text{ cm}^{-1}$  in the IR spectra of the isatin-bishydrazone ligands are assigned to  $\nu$ (C=N) and  $\nu$ (HC=N), respectively. In comparison with the spectra of the isatin-bishydrazone ligands, all the Ni(II) complexes exhibited the band of  $\nu$ (HC=N) in the region of  $\approx$ 1590 cm<sup>-1</sup>, showing the shift of the band to lower wave numbers, indicating that the azomethine nitrogen is coordinated to the metal ion [25,26]. The band of  $\nu$ (C=O) in the region of 1670– 1680 cm<sup>-1</sup> in the metal complexes showing the shift to lower wave numbers confirms that the carbonyl oxygen is coordinated to the metal ion [27]. The unaltered position of a band due to  $\nu(NH)$  and  $\nu(C=N)$  in all the metal complexes indicates that these groups are not involved in coordination. The new bands in the region of 500–510 and 630–650  $\text{cm}^{-1}$  in the spectra of the complexes are assigned to stretching frequencies of (M-N) and (M–O) bonds, respectively [28]. Thus, the IR spectral results provide strong evidences for the complexation of Isatin-bishydrazone ligands with the metal ion in the tridentate mode via isatin-carbonyl (C=O), azomethine-N (C=N), and pyridine-N (C = N).

*Electronic Spectra.* The absorption maxima bands are listed in Table II and the spectra are given in Fig. 1. The UV–vis spectra of the isatin-bishydrazone ligand show



Figure 1 UV-vis spectra of the Ni(II) isatin-hydrazone complexes.

Complex	Step	TG <sub>range</sub> (°C)	DTA <sub>max</sub> (°C)	Thermal Effect	Mass Loss Observed (Calculated) (%)	Assignment	Metallic Residue
Ni-cpish complex	Ι	53.11-106.55	78.38	Endo	8.98 (8.30)	2H <sub>2</sub> O (hydrated)	
	Π	106.55-426.69	209.42	Endo	5.13 (4.14)	1H <sub>2</sub> O (coordinated)	
	III	426.69-600.53	506.16	Endo	58.10 (57.68)	Organic moiety	NiCl <sub>2</sub>
Ni-apish complex	Ι	54.07-219.16	78.71	Endo	8.55 (8.03)	2H <sub>2</sub> O (hydrated)	
	II	219.16-389.07	196.61	Endo	5.22 (4.02)	1H <sub>2</sub> O (coordinated)	
	III	389.07-497.8	460.33	Endo	75.11 (72.86)	Organic moiety	NiCl <sub>2</sub>
Ni-bpish complex	Ι	56.07-210.55	87.68	Endo	7.35 (7.06)	2H <sub>2</sub> O (hydrated)	
	II	210.55-404.91	265.57	Endo	4.05 (3.53)	1H <sub>2</sub> O (coordinated)	
	III	404.91-580.93	519.39	Endo	65.78 (63.99)	Organic moiety	NiCl <sub>2</sub>

Table III Thermoanalytical Data (TG, DTG): Ni(II) complexes

**Table IV** Observed First-Order Rate Constants,  $k_{obs}$  (s<sup>-1</sup>), Derived Second-Order Rate Constants  $k_2$  (10<sup>3</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>), and Transfer Free Energies of Activation,  $\delta_m \Delta G^{\neq}$  (KJ mol<sup>-1</sup>) for Acid-Catalyzed Aquation of Ni-cpish, Ni-apish, and Ni-bpish complexes at 4.50 × 10<sup>-4</sup> M in Different Water-Methanol Binary Mixtures and I<sub>NaCl</sub> = 0.16 mol dm<sup>-3</sup> at T = 298 K

			[H <sup>+</sup> ] (m	ol dm $^{-3}$ )			
		0.14	0.1	0.06	0.02		
MeOH (vol%)			$10^{4} k_{\rm ol}$	$(s^{-1})$		$k_2 \ 10^3 \ (\mathrm{dm^3 \ mol^{-1} \ s^{-1}})$	$\delta_m \triangle G^{\neq} \; (\mathrm{KJ} \; \mathrm{mol}^{-1})$
Ni-cpish complex	0	26.6	19	11.4	3.79	18.965	_
	20	13.1	9.39	5.63	1.88	9.389	1.742864
	40	3.93	2.81	1.69	0.562	2.81	4.732828
	60	1.18	0.841	0.505	0.168	0.841	7.722791
Ni-apish complex	0	8.26	5.9	3.54	1.18	5.9	_
	20	3.46	2.47	1.48	0.494	2.47	2.158564
	40	1.03	0.739	0.444	0.148	0.739	5.148528
	60	0.31	0.221	0.133	0.0443	0.221	8.138491
Ni-bpish complex	0	2.57	1.84	1.1	0.367	1.835	_
	20	0.91	0.65	0.39	0.13	0.65	2.573874
	40	0.272	0.194	0.117	0.0389	0.194	5.563838
	60	0.0815	0.0582	0.0349	0.0116	0.0582	8.553801

important strong bands at  $\approx 388$  and  $\approx 230$  nm due to  $\pi - \pi^*$  and  $n - \pi^*$  transitions [25] respectively. These bands are altered to a greater extent on complexation. The spectrum of Ni(II)-complexes shows characteristic bands at  $\lambda_{\text{max}} \approx 670-680$  nm due to d–d transition.

Thermogravimetric Analysis of the Prepared Isatin-Bishydrazone Complexes. Thermal data of the complexes are given in Table III. The Ni(II) complexes of the Isatin-bishydrazone ligands exhibited thermal stability in the range of  $\approx 25-50^{\circ}$ C, and then degrade in three steps (cf. Figs. 1a–1c in the Supporting Information). The first degradation step in the temperature range  $\approx 350-360$  K may account for the loss of the hydrated water molecules (two water molecules). The second degradation step in the temperature range  $\approx$ 470–540 K may be attributable to the loss of the coordinated water molecule (one water molecule), and the third step of decomposition occurs within the temperature range  $\approx$ 730–790 K corresponding to the loss of the organic moiety leaving NiCl<sub>2</sub> as metallic residue.

## Acid-Catalyzed Aquation of Ni(II) Complexes

The observed first-order rate constants ( $k_{obs}$ ) as a function on [H<sup>+</sup>] and in the presence of different watermethanol and water-acetone ratios were calculated from the dependence of absorbance on time at the appropriate  $\lambda_{max}$  for the investigated compounds using Microcal Origin program version 7.5 (cf. Tables IV

**Table V** Observed First-Order Rate Constants,  $k_{obs}$  (s<sup>-1</sup>), Derived Second-Order Rate Constants,  $k_2$  (10<sup>3</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>), and Transfer Free Energies of Activation,  $\delta_m \Delta G^{\neq}$  (KJ mol<sup>-1</sup>) for Acid-Catalyzed Aquation of Ni-cpish, Ni-apish, and Ni-bpish complexes at 4.50 × 10<sup>-4</sup> M in Different Water–Acetone Binary Mixtures and I<sub>NaCl</sub> = 0.16 mol dm<sup>-3</sup> at T = 298 K

			[H <sup>+</sup> ] (m	ol dm $^{-3}$ )			
		0.14	0.1	0.06	0.02		
Acetone (vol%)			$10^{4} k_{\rm ob}$	$_{0.05}$ (s <sup>-1</sup> )		$k_2 \ 10^3 \ (\mathrm{dm^3 \ mol^{-1} \ s^{-1}})$	$\delta_m \triangle G^{\neq} \; (\mathrm{KJ} \; \mathrm{mol}^{-1})$
Ni-cpish complex	0	18.2	14.6	5.4	2.62	13	_
	20	13	10.4	3.86	1.87	10.4	0.537016
	40	7.78	6.26	2.32	1.12	3.86	3.001621
	60	2.59	2.09	0.772	0.374	1.87	4.795782
Ni-apish complex	0	6.86	4.65	1.62	0.744	4.9	_
	20	4.9	3.32	1.16	0.531	3.32	0.964516
	40	2.94	1.99	0.696	0.319	1.16	3.571156
	60	0.98	0.664	0.232	0.106	0.531	5.50426
Ni-bpish complex	0	2.57	1.36	0.419	0.223	1.84	_
	20	1.84	0.97	0.299	0.159	0.97	1.580713
	40	1.1	0.582	0.18	0.0955	0.299	4.491745
	60	0.367	0.194	0.0599	0.0318	0.159	6.057015

and V), showing that the values of  $k_{obs}$  decreased as the proportion of co-organic solvent increases. This may be due to the salting out of the hydrophilic H<sup>+</sup> and stabilization of the studied compound. The dependence of  $k_{obs}$  on the acid concentration is linear for all the Ni(II)-isatin-bishydrazone complexes in the co-organic (methanol and acetone) solvent without a significant intercept (cf. Figs. 2 and 3), hence the hydrolysis follows the rate law with

$$k_{\rm obs} = k_2 [\rm H^+]$$

where  $k_2$  is the second-order rate constant at  $[H^+] >>$  [compound]. This equation indicates that the second-order process is dominant in the present solvent mixtures. Values of  $k_2$  are cited in Tables IV and V.

The change in the activation barrier,  $\delta_m \Delta G^{\#}$ , of the investigated compounds from water to water–methanol and from water to water–acetone mixtures is evaluated and reported in Tables IV and V from the ratio of rate constants of the acid hydrolysis in the aqueous-solvent ( $k_{2S}$ ) to the corresponding values in the aqueous solution ( $k_{2W}$ ) according to the following relation [29]:

$$\delta_m \Delta G^{\#} = -RT \ln \left( \frac{k_{2s}}{k_{2w}} \right)$$

It is observed that the values of  $\delta_m \Delta G^{\#}$  increase with the increasing of the methanol content (cf. Fig. 4), and these values matches with the decreasing of  $k_{obs}$  (cf. Figs. 2 and 3) and  $k_2$  (cf. Fig. 5) values as the methanol or acetone content increases.

The Mechanism of the Acid-Hydrolysis. The characteristic band for the investigated complexes in the UV-vis spectra lies at  $\lambda_{max} = 625-680$  nm. But on addition of the acid, a redshift occurred at the  $\lambda_{max}$ of the investigated complex (cf. Fig. 6), then this new band decays by the first-order kinetics in [complex]. This spectrophotometric behavior illustrates with the naked eye observation that a rapid change occurs in the color of the complex, from dark red to violet, and then fades slowly. These spectrophotometrically and visually observable acts would suggest the following mechanism for the acid aquation of the recent complexes (cf. Scheme 2): In the recent acidic medium  $(pH \le 2)$ , the aquation rates of these compounds increase with decreasing pH. Thus, in these solutions, the aquation mechanism would involve the conversion of the azomethine group (-RC=N-) group to its conjugate acid (-RC=NH<sup>+</sup>-) by a rapid preequilibrium followed by a slow attack of water. This argument has a reasonable theoretical basis that the azomethine carbon assumes considerable carbonium ion characteristics induced by conjugate acid formed in these acidic media and that it is more susceptible to nucleophilic attack by water [30]. After this, the protonated complex decays rapidly into the final products of the reaction (cf. Scheme 2).



**Figure 2** Plots of the observed first-order rate constants of the reaction between HCl and Ni-complexes as a function of  $[H^+]$  in different water-methanol mixtures at  $[complex] = 1 \times 10^{-4}$  M, I = 0.1 M, and 298 K: (a) Ni-cpish complex, (b) Ni-apish complex, and (c) Ni-bpish complex.

**Solvent Effects.** The solvent effect of the acidcatalyzed aquation on the investigated complexes could be presented by plotting logarithms of the rate constant quotients in water–methanol mixtures,  $k_{2(s)}/k_{2(w)}$ , against volume% methanol (cf. Fig. 7). The rate constants decrease with increasing of the methanol or ace-



Figure 3 Plots of the observed first-order rate constants of the reaction between HCl and Ni-complexes as a function of  $[H^+]$  in different water–acetone mixtures at [complex] = 1  $\times 10^{-4}$  M, I = 0.1 M, and 298 K: (a) Ni-cpish complex, (b) Ni-apish complex, and (c) Ni-bpish complex.

tone content for all Ni(II) complexes. The Ni-cpish complex is considerably more reactive than the Ni-apish complex and Ni-bpish complex toward the acid aquation in aqueous media. This reactivity order could be explained according to the hydrophobic/hydrophilic nature of the ligands with substituents R groups, from



**Figure 4** Dependence of the activation barrier  $\delta_m \triangle G^{\neq}$  on the solvent composition for acid aquation of Ni(II)-isatin-hydrazone complexes: (a) in different water–methanol mixtures and (b) in different water–acetone mixtures.

R = H,  $CH_3$  to ph in cpish, apish to bpish, respectively. The more hydrophilic complex (Ni-cpish, R =H) is more reactive than the less hydrophilic ligands (Ni-apish and Ni-bpish,  $R = CH_3$  and ph, respectively) in aqueous media. By increasing the methanol ratio in the acid dissociation reaction, the reactivity of the more hydrophilic complex, Ni-cpish, is highly decreased and oppositely it took place for the less hydrophilic complexes, Ni-apish and Ni-apish.

## CONCLUSIONS

Some new Ni(II) Isatin-bishydrazone complexes have been synthesized and characterized. To gain more information about the kinetic behavior of the acid aquation of these complexes, it was followed spectrophotometrically, with describing the effects of methanol



Figure 5 Dependence of the rate constant  $(k_2)$  on the solvent composition for acid aquation of Ni(II)-isatin-hydrazone complexes: (a) in different water–methanol mixtures and (b) in different water–acetone mixtures.



**Figure 6** Repeated spectral scans of the Ni-bpish complex at  $[H^+] = 0.06$  M, [Ni-bpish complex] =  $1 \times 10^{-4}$  M, I = 0.16 M, and 298 K, with an interval time = 2 min.



Scheme 2 Schematic diagram of acid hydrolysis of the Ni(II)-isatin-bishydrazone complexes.



Figure 7 Dependence of rate constants on solvent composition for acid aquation of Ni(II)-isatin-hydrazone complexes.

and acetone as organic cosolvents, on the kinetics of the acid aquation of these complexes at 298 K, also the second rate constant ( $k_2$ ) in addition to evaluate the change in the activation barrier of the investigated compounds. Finally, the mechanism of the acid aquation of these complexes was suggested. Methanol and acetone have been chosen as a cosolvent due to the availability previously measured chemical potentials, which aided in interpretation of the rate constant data.

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