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Synthesis and Physico-Chemical Properties of Some Ni(II) Complexes with Isatin-Hydrazones[1]

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Abstract—New Ni(II) complexes with bioactive bishydrazones ligands based on (pyridine-2-carboxaldhyde)-3-isatin, (2-acetylpyridine)-3-isatin, and (2-benzoylpyridine)-3-isatin have been synthesized and characterized by elemental analysis, conductivity measurements, IR and UV-Vis spectroscopy, and thermal analysis. The complexes stoichiometry and formation constants have been determined. The results suggest that isatin-bishydrazones act as neutral tridentate ligands with ONN sites coordinating to the metal ion via isatin C=O, azomethine CR=N, and pyridine C=N groups to give $[Ni(L)H_2O]Cl_2{\cdot}2H_2O$, (L = neutral tridentate isatin hydrazone ligand). Kinetics and thermodynamic parameters of the complexes thermal decomposition have been elucidated from the thermal data using Coats and Redfern method, which has confirmed the first order kinetics.

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The preparation of new ligands is perhaps the most efficient approach to develop metal complexes exhibiting unique properties and novel reactivity. The Schiff's bases are important class of ligands widely applied in biology, clinical medicine, analytical chemistry, catalysis, organic synthesis, and industry [1]. A considerable number of the Schiff's bases complexes are of potential interest as biological models in understanding the structure of biomolecules and related processes [2]. The Schiff's bases ligands containing various donor atoms (N, O, S, etc.) show broad range of biological activity that can be enhanced or altered due to variety of ways the ligands can be bound to metal ions [3]. Recently, metal compounds containing isatin moiety have received a great deal of attention in the fields of inorganic chemistry, biochemistry and environmental chemistry. Among heterocyclic compounds, isatin and its derivatives have revealed remarkable biological activity [4–9], as well as metal complexes with the Schiff's bases of isatin derivatives [10–12]. Although much attention has been directed to studies of the metal complexes of the Schiff's base ligands derived from isatin [13, 14], no investigations have appeared in the literature on the metal complexes of the Schiff's bases derived from isatin monohydrazone and 2-substituted pyridines. In order to fill in the gap, we prepared and characterized such new isatin-bishydrazone compounds that showed notable biological activity [15]. In the present work, we aimed to synthesize the new Ni(II) complexes with the bioactive isatin-bishydrazone ligands and to characterize them with a variety of physico-chemical methods.

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

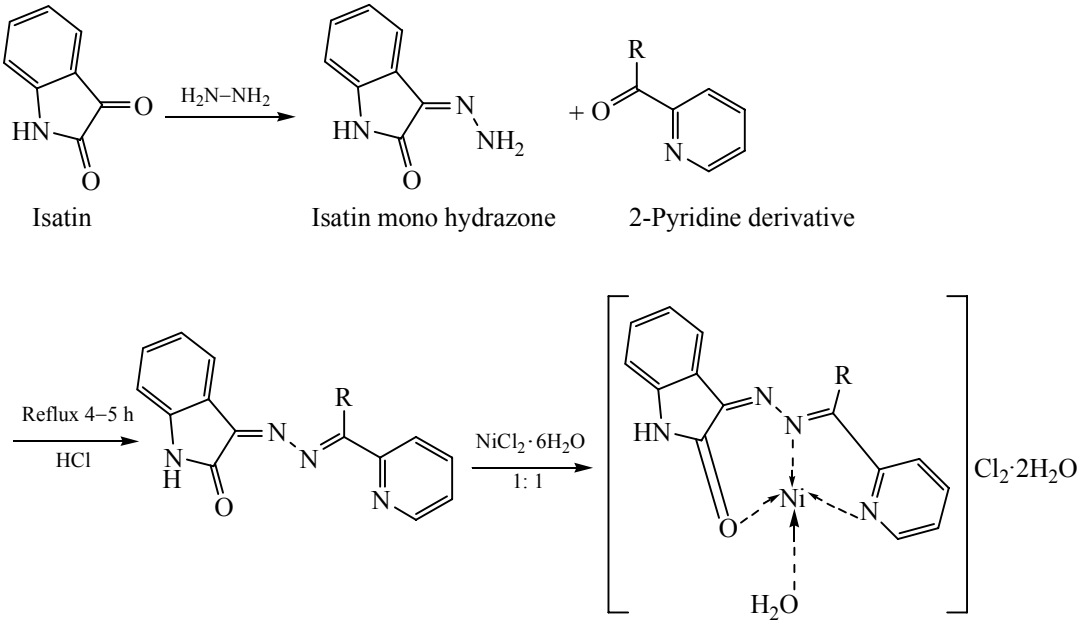
The results of the elemental microanalysis of the prepared isatin bishydrazone ligands and their Ni(II) complexes are reported in Table 1 together with the respective molar conductivity. The results suggested that the bishydrazones acted as neutral tridentate ligands to form the complexes at 1 : 1 metal to ligand molar ratio, all the complexes being 1 : 2 electrolytes [25, 26]. Thus, the following general formula of the prepared complexes was derived: $[Ni(L)(H_2O)]Cl_2{\cdot}2H_2O$, and the complexes were formed according to the equation

$$NiCl_2{\cdot}6H_2O + L \rightarrow [Ni(L)(H_2O)]Cl_2{\cdot}2H_2O + 3H_2O$$

with L being the isatin bishydrazone ligand. The results shown in Table 1 coincided well with the expected complexes composition, thus additionally confirming the purity of the prepared ligands and the complexes.

[1] The text was submitted by the authors in English.

Scheme 1.



Isatin Isatin mono hydrazone 2-Pyridine derivative

Ni(II) complex

Ligand		Metal	Complex	
R	Abbrev.		Abbrev.	Empirical formula
H	cpish	Ni(II)	Ni(cpish)	$[Ni(cpish)(H_2O)]Cl_2 \cdot nH_2O$
CH_3	apish	Ni(II)	Ni(apish)	$[Ni(apish)(H_2O)]Cl_2 \cdot nH_2O$
Ph	bpish	Ni(II)	Ni(bpish)	$[Ni(bpish)(H_2O)]Cl_2 \cdot nH_2O$

Unfortunately we could not take advantage of the powerful structure elucidation technique, X-ray diffraction; however we recorded the infrared spectra in order to elucidate the nature of the ligands to metal ion bonding. The major infrared absorption bands of the subject ligands and their metal complexes are collected in Table 2. The observed bands could be classified into those originating from the ligand vibrations and those arising from the bonds between metal ions and the ligand coordinating sites. The IR subspectra corresponding to the isatin bishydrazone ligands revealed the characteristic bands of ν(N–H) (3180–3200 cm^{-1}) and of lactone carbon ν(C=O) (1722 cm^{-1}), ν(C=N) (1460 cm^{-1}), ν(CH=N) (1621 cm^{-1}) [27]. As compared with the spectra of the isatin bishydrazone ligands, those of all the Ni(II) complexes revealed the ν(HC=N) band at about 1590 cm^{-1}; the observed band shift to lower wavenumbers indicated that the azomethine nitrogen was coordinated to the metal ion [19, 20]. Similarly, the complexes ν(C=O) band in the region of 1670–1680 cm^{-1} (shifted to lower wavenumbers), confirming that the isatin carbonyl oxygen was coordinated to the metal ion as well [20, 21]. The unchanged position of the ν(N–H) and ν(C=N) bands in the cases of all the metal complexes indicated that those groups were not involved in coordination. The newly appeared bands in the 500–510 cm^{-1} and 630–650 cm^{-1} regions in the spectra of the complexes were assigned to ν(Ni–N) and ν(Ni–O), respectively [22]. Thus, the IR spectral studies provided strong evidences for the complexation of isatin bishydrazone ligands with metal ion in via isatin carbonyl oxygen (C=O), azomethine nitrogen (C=N), and pyridine nitrogen (C=N); therefore isatin bishydrazone acted as tridentate ligand.

The major features of electronic absorption spectra of the isatin bishydrazone ligands and their complexes with Ni(II) (recorded in methanol media, $c = 1 \times 10^{-3}$ mol/L, at 298 K) are listed in Table 2 as well. In the spectra of the ligands, the strong bands at about 388 and at about 230 nm were assigned to π–π^* and n–

Table 1. Physical data and elemental analysis of the ligands and the complexes

Complex	Empirical formula (formula weight)	Color	mp, °C	Yield, %	Elemental analysis found (calculated)					Molar condictivity μ_v ($\Omega^{-1}cm^2\ mol^{-1}$) in the respective solvent		
					C %	H %	N %	Cl %	Ni %	methanol	DMF	ethanol
cpish	$C_{14}H_{10}N_4O$ (250.255)	Red	245	89	67.19 (67.20)	4.03 (4.33)	22.39 (22.30)	–	–	–	–	–
Ni(cpish)	[Ni(cpish) H_2O]$Cl_2 \cdot 2H_2O$ (433.89)	Dark brown	> 300	65	38.84 (38.75)	3.49 (3.72)	12.94 (12.91)	16.38 (16.34)	13.56 (13.53)	170	140	85
apish	$C_{15}H_{12}N_4O$ (264.28)	Red	250	85	68.17 (68.50)	4.58 (4.25)	21.20 (20.98)	–	–	–	–	–
Ni(apish)	[Ni(apish) H_2O]$Cl_2 \cdot 2H_2O$ (447.93)	Dark brown	> 300	60	40.31 (40.22)	3.83 (4.05)	12.54 (12.51)	15.87 (15.83)	13.13 (13.10)	166	137	82
bpish	$C_{20}H_{14}N_4O$ (326.35)	Red	265	85	73.61 (73.55)	4.32 (4.28)	17.17 (17.05)	–	–	–	–	–
Ni(bpish)	[Ni(bpish) H_2O]$Cl_2 \cdot 2H_2O$ (509.99)	Dark brown	> 300	70	47.29 (47.10)	3.57 (3.95)	11.03 (10.99)	13.96 (13.90)	11.55 (11.51)	160	133	80

Table 2. Infrared absorption bands frequencies (cm^{-1}) and electronic absorption spectra features of the isatin bishydrazone ligands and their metal complexes

Complex	Frequency of infrared vibration (cm^{-1})							Electronic spectra		
	ν(O–H)[a]	ν(N–H)[b]	ν(C=O)[c]	ν(HC=N)[d]	ν(C=N)[e]	ν(Ni–O)	ν(Ni–N)	λ_{max}, nm	ε (λ_{max}) (L mol^{-1} cm^{-1})	Assignment
cpish	3421.2	3276.5	1721.7	1613.7	1460.3	–	–	237	1744.05	π–π^*
								324	865.49	n–π^*
Ni(cpish)	3430.8	3287.1	1685.0	1611.7	1409.0	656.8	510.2	627	320.12	d–d
								676	293.02	d–d
apish	3393.2	3180.0	1721.7	1618.5	1458.4	–	–	254	538.30	π–π^*
								274	580.97	π–π^*
								325	339.05	n–π^*
Ni(apish)	3357.5	3159.8	1672.5	1592.4	1463.2	637.6	504.4	625	723.22	d–d
								680	256.57	d–d
bpish	3424.0	3181.0	1721.7	1607.9	1452.6	–	–	252	1096.47	π–π^*
								271	882.56	π–π^*
								327	653.87	n–π^*
Ni(bpish)	3359.4	3160.7	1671.5	1594.4	1463.2	636.6	503.5	636	268.80	d–d
								682	295.95	d–d

[a] OH of water molecules. [b] Indole ring (N–H). [c] Lactone group (C=O). [d] Azomethine group (C=N). [e] β-Hydrazone of isatin (C=N).

π^* transitions, respectively [19]. Positions of those bands were much changed upon complexation. The spectra of the Ni(II) complexes showed up characteristic bands at λ_{max} of about 670–680 nm due to *d–d* transition.

In addition to the elemental analysis data reported in Table 1, the stoichiometry of the Ni(II) complexes with isatin bishydrazone could be determined by spectrophotometric molar ratio [23–25] or continuous variation [26, 27] methods. Their application to the studied systems confirmed the 1: 1 metal to ligand molar ratios as documented in Fig. 1 (continuous variation method) and Fig. 2 (molar ratio method).

The equilibrium constants of the complexes formation constants K_f were determined from the spectrophotometric measurements according to the following equation derived from the continuous variation method [28]:

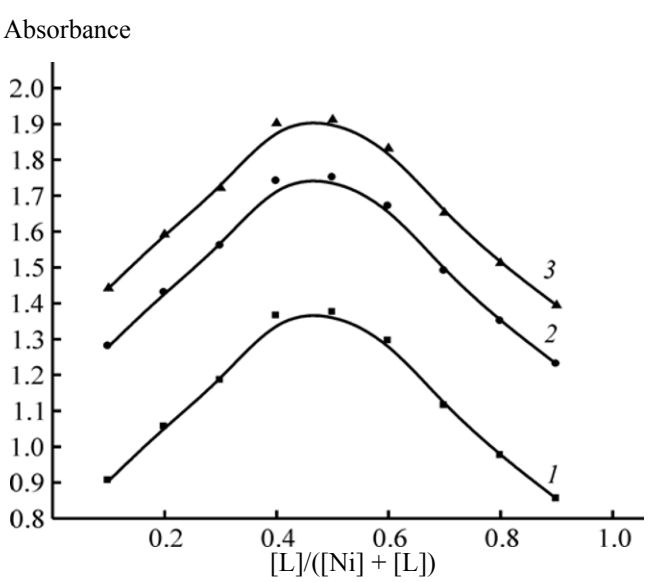


Fig. 1. Determination of composition of the isatin bishydrazone complexes with Ni(II) by continuous variation method: (*1*) [Ni(cpish)(H_2O)]Cl_2·nH_2O, (*2*) [Ni(apish)(H_2O)]Cl_2·nH_2O, and (*3*) [Ni(bpish)(H_2O)]Cl_2·nH_2O.

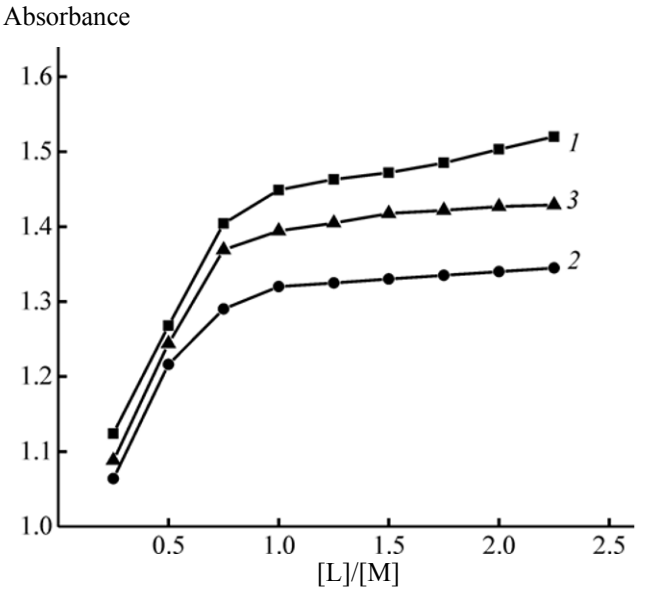


Fig. 2. Determination of composition of the isatin bishydrazone complexes with Ni(II) by molar ratio method: (*1*) [Ni(cpish)(H_2O)]Cl_2·nH_2O, (*2*) [Ni(apish)(H_2O)]Cl_2·nH_2O, and (*3*) [Ni(bpish)(H_2O)]Cl_2·nH_2O.

$$K_f = \frac{\frac{A}{A_m}}{\left(1 - \frac{A}{A_m}\right)^2 C}$$

with A_m being the absorbance at the point of the most complete complex formation, A being the absorbance of the complex at the arbitrary chosen metal ion concentration C. The derived data collected in Table 3 indicated the high stability of the prepared complexes. The values of K_f for the studied complexes decreased in the following series: Ni(bpish) > Ni(apish) > Ni(cpish).

From the equilibrium formation constant measured at different temperatures, we managed to determine the thermodynamic parameters of the complexes formation. According to the Gibbs–Helmholtz equation, by plotting the log K_f values as function of (1/T), from the slope of the linear plot we got $\Delta_f H$, and $\Delta_f S$ was determined from the intercept (Fig. 3). The derived parameters are given in Table 3.

The negative values of $\Delta_f G$ reflected that the complex formation was spontaneous under all the studied conditions. As $\Delta_f H$ was negative, the reaction was exothermic, and the formed metal-ligand bonds were fairly strong. The positive entropy changes were due to the release of bound water molecules from the metal chelates [29] according to the following generalized equation:

$$[M(H_2O)_x]^{n+} + L \rightarrow [(L)M(H_2O)_m]^{n+} + (x - m)H_2O.$$

Thermal measurements can give important information on the complexes structure, the number of

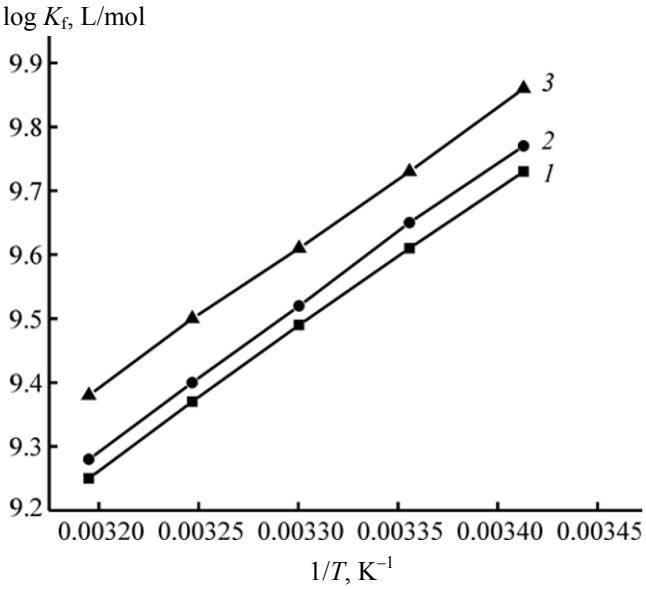


Fig. 3. Determination of thermodynamic parameters of the complexes formation from log K_f data. (*1*) Ni(cpish), (*2*) Ni(apish), and (*3*) Ni(bpish).

Table 3. Stability constants and thermodynamic parameters of the complexes formation

Complex	T, °C	K_f (×10^9), L/mol	log K_f	$\Delta_f H$, kJ/mol	$\Delta_f S$, J mol^{-1} K^{-1}	$\Delta_f G$, kJ/mol
Ni(cpish)	20	5.34	9.73	–42.1	0.0426	–54.6
	25	4.09	9.61			–54.8
	30	3.08	9.49			–55.0
	35	2.34	9.37			–55.2
	40	1.77	9.25			–55.5
Ni(apish)	20	5.89	9.77	–43.2	0.0397	–54.8
	25	4.47	9.65			–55.0
	30	3.35	9.52			–55.2
	35	2.53	9.40			–55.4
	40	1.93	9.28			–55.6
Ni(bpish)	20	7.20	9.86	–41.8	0.0461	–55.3
	25	5.43	9.73			–55.5
	30	4.09	9.61			–55.8
	35	3.14	9.50			–56.0
	40	2.39	9.38			–56.2

hydrated and coordinated water molecules. Thermal data related to the studied complexes are given in Table 4. The complexes were thermally stable at 25–50°C, and degraded in three steps at higher temperature (Fig. 4). The first degradation step at 350–360 K could be due to the loss of the two hydrating water molecules; the second degradation step at 470–540 K was assigned to the loss of the one coordinated water molecule; and the third step of decomposition at 730–790 K corresponded to the burning out of organic part of the complex leaving $NiCl_2$ as inorganic residue.

The kinetic and thermodynamic parameters of the decomposition steps (activation energy $\Delta E^{\#}$, enthalpy of activation $\Delta H^{\#}$, entropy of activation $\Delta S^{\#}$, and free energy change of decomposition $\Delta G^{\#}$) were evaluated by using the Coats–Redfern relation [30]:

$$\log\left[-\log\frac{1-\alpha}{T^2}\right] = \frac{\log AR}{\alpha E^{\#}}\left[1-\frac{2RT}{E^{\#}}\right]-\frac{E^{\#}}{2.3RT}$$

with α being the conversion of decomposition at temperature T, $E^{\#}$ the activation energy, β the linear heating rate, A the Arrhenius constant, and other parameters having their usual meaning; $(1 - 2RT/E^{\#}) \approx 1$. The plot in the Coats-Redfern coordinates shown in Fig. 5 confirmed the first-order kinetics; $E^{\#}$ was determined from the lot slope and A was derived from the intercept. The thermodynamic parameters of decomposition activation were calculated as follows [31, 32]:

$$\Delta S^{*} = 2.303R\log\left[\left(\frac{Ah}{k_B T_s}\right)\right],$$

$$\Delta H^{*} = E_a - RT_s,$$

$$\Delta G^{*} = \Delta H^{*} - T\Delta S^{*},$$

where h being the Planck's constant, T_s the peak decomposition temperature, and k_B the Boltzmann constant. The so derived parameters are collected in Table 5. From the table, the negative activation entropy was somewhat compensated by the enthalpy of activation, thus giving the very close values of the free energy of activation for all the three complexes [33]. The high values of the activation energy reflected the thermal stability of the complexes. Overall, the data clearly indicated similarity in the thermal degradation of the studied complexes.

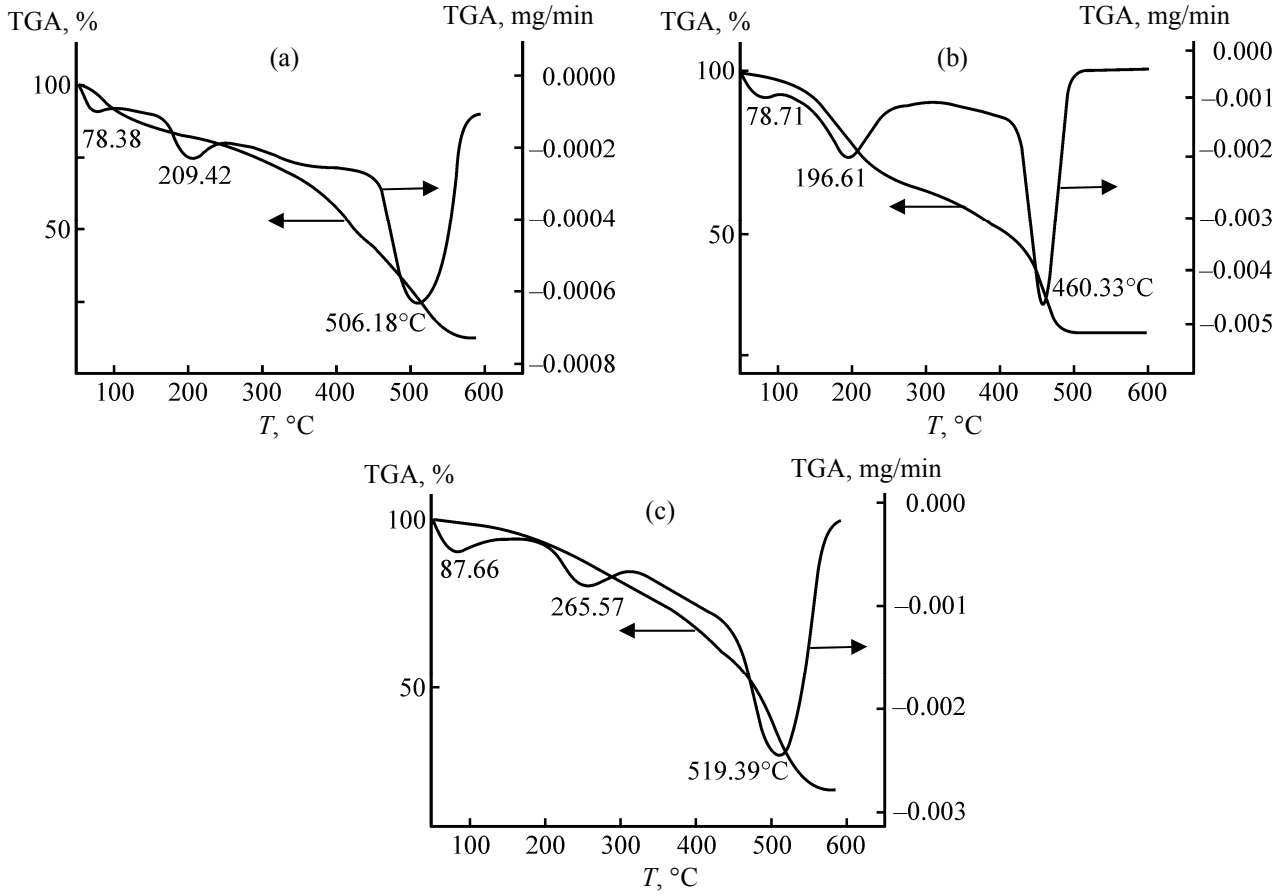


Fig. 4. Thermal decomposition of the complexes: (a) $[Ni(cpish)(H_2O)]Cl_2 \cdot 2H_2O$, (b) $[Ni(apish)(H_2O)]Cl_2 \cdot 2H_2O$, and (c) $[Ni(bpish)(H_2O)]Cl_2 \cdot 2H_2O$.

EXPERIMENTAL

All the chemicals were used as received without further purification. Isatin, 2-acetylpyridine, 2-benzoylpyridine, and pyridine-2-carboxaldhyde were obtained from Sigma-Aldrich. Hydrazine hydrate and hydrated nickel chloride ($NiCl_2 \cdot 6H_2O$) were obtained from BDH. Other reagents and solvents (methanol, ethanol, and dimethylformamide) were purchased from local supplier and were of analytical pure grade.

Synthesis of the ligands. Isatin-bishydrazone ligands, bishydrazones of (pyridine-2-carboxaldhyde)-3-isatin (cpish), (2-acetylpyridine)-3-isatin (apish), and

Table 4. TGA data of the studied complexes

Complex	Step	Temperature range, °C	Extreme temperature, °C	Thermal effect	Mass loss: observed (calculated), %	Assignment	Residue
Ni(cpish)	I	53–106.5	78.38	*endo*	8.98 (8.30)	$2H_2O$ (hydrated)	$[Ni(cpish)(H_2O)]Cl_2$
	II	106.5–427	209.42	*endo*	5.13 (4.14)	$1H_2O$ (coordinated)	$[Ni(cpish)]Cl_2$
	III	427–600.5	506.16	*endo*	58.10 (57.68)	Organic moiety	$NiCl_2$
Ni(apish)	I	54–219	78.71	*endo*	8.55 (8.03)	$2H_2O$ (hydrated)	$Ni(apish)(H_2O)]Cl_2$
	II	219–389	196.61	*endo*	5.22 (4.02)	$1H_2O$ (coordinated)	$[Ni(apish)]Cl_2$
	III	389– 498	460.33	*endo*	75.11 (72.86)	Organic moiety	$NiCl_2$
Ni(bpish)	I	56–210.5	87.68	*endo*	7.35 (7.06)	$2H_2O$ (hydrated)	$Ni(bpish)(H_2O)]Cl_2$
	II	210.5–405	265.57	*endo*	4.05 (3.53)	$1H_2O$ (coordinated)	$[Ni(bpish)]Cl_2$
	III	405–581	519.39	*endo*	65.78 (63.99)	Organic moiety	$NiCl_2$

Table 5. The activation parameters of decomposition steps as derived from TGA

Complex	Order	Step	$E^{\#}$, kJ/mol	A, s^{-1}	$\Delta S^{\#}$, J K^{-1} mol^{-1}	$\Delta H^{\#}$, kJ/mol	$\Delta G^{\#}$, kJ/mol
Ni(cpish)	1	I	49.255	494185.73	–137.29	46.333	94.576
		II	8.386	124409.39	–151.40	4.375	77.414
		III	12.859	127856.08	–155.15	6.381	127.275
Ni(apish)	1	I	51.593	496722.47	–137.26	48.669	96.945
		II	43.955	53371.46	–158.21	40.051	114.350
		III	136.150	390861.98	–145.36	130.053	236.652
Ni(bpish)	1	I	40.780	53708.27	-155.967	37.782	94.036
		II	40.254	11163.51	–172.363	35.776	128.606
		III	61.315	13620.96	–173.920	54.727	192.539

(2-benzoylpyridine)-3-isatin (bpish) were prepared in two steps as described in [15]: preparation of isatin monohydrazone followed by condensation with the 2-pyridine derivative.

*Synthesis of Isatin-monohydrazone***.** Solution of isatin (1.47 g, 10 mmol) in methanol (40 mL) was added to solution of hydrazine hydrate (0.05 g, 10 mmol) hot methanol (5 mL). The resulting mixture was refluxed during 3 h on a water bath. Upon cooling, the yellow product was precipitated; it was filtered off, washed with cold methanol, dried, and recrystallized from methanol [34].

*Synthesis of isatin bishydrazones***.** 1.0 mmol of the respective 2-substituted pyridine (2-acetylpyridine, 2-benzoylpyridine, or pyridine-2-carboxaldhyde) was added dropwise to a hot solution of isatin-monohydrazone (1.0 mmol) in methanol. The resulting mixture was refluxed during 1 h upon stirring, then 2–3 drops of glacial acetic acid was added, and refluxing was continued during further 4 h upon stirring. After cooling, the bishydrazone was precipitated; it was filtered off, washed with cold methanol, dried, and recrystallized from methanol [15].

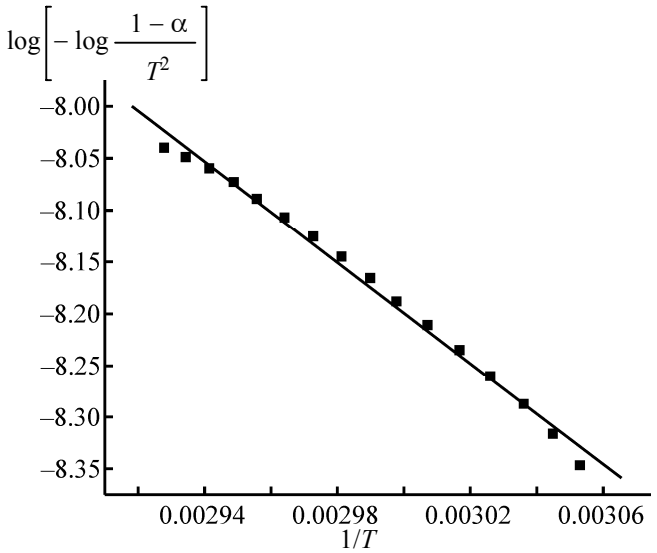


Fig. 5. The Coats-Redfern plot and its linear fit in the case of $[Ni(cpish)(H_2O)]Cl_2 \cdot 2H_2O$ complex.

*Synthesis of Ni(II) complexes with isatin bis-hydrazones***.** Solution of $NiCl_2 \cdot 6H_2O$ (1.0 mmol) in minimal amount of water was added dropwise to hot solution of the ligand (1.0 mmol of cpish, apish, or bpish) in methanol. The resulting mixture was refluxed at 70°C during 10 h under constant stirring. After partial evaporation overnight, the resulted solid product was filtered off, washed with water-methanol mixture, dried, and recrystallized from water-methanol mixture. Yield and melting point were determined for each product.

Characterization. The complexes composition was derived from C, H, and N content as determined with Perkin-Elmer 40c elemental analyzer (Micro-analytical Centre at Cairo University, Egypt). The molar conductance of 10^{-3} mol/L solutions was measured with JENWAY 4320 conductometer at 298 K. IR spectra were recorded with Shimadzu FTIR 8101 at 4000–400 cm^{-1} (KBr).

Electronic absorption spectra of the complexes in methanol were recorded with Jasco V-530 spectrophotometer (200–800 nm, 10 mm quartz cell). The spectrometer thermostatted cell holder was supplied by an ultrathermostat water circulator (CRIOTERM 190) to control the temperature within 0.1°C at 20–40°C.

Rigaku 8150 thermo-analyzer was used for simultaneous recording of TGA and DTA curves at heating rate of 10 K min^{-1}.

The stoichiometry of the complexes and their formation constants were determined using the spectrophotometric molar ratio [23–25] and continuous variation [26, 27] methods. In order to estimate thermodynamic parameters of the prepared complexes, the continuous variation method measurements were performed at 20–40°C.

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