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# Spectroscopic, thermal and electrochemical studies on some nickel(II) thiosemicarbazone complexes

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#### Abstract

Several complexes of thiosemicarbazone derivatives with Ni(II) have been prepared. Structural investigation of the ligands and their complexes has been made based on elemental analysis, magnetic moment, spectral (UV–Vis, i.r., <sup>1</sup>H NMR, ms), and thermal studies. The i.r. spectra suggest the bidentate mononegative and tridentate (neutral, mono-, and binegative) behavior of the ligands. Different stereochemistries were suggested for the isolated complexes. The thermogravimetry (TG) and derivative thermogravimetry (DTG) have been used to study the thermal decomposition and kinetic parameters of some ligands and complexes using the Coats-Redfern and Horowitz-Metzger equations. The redox properties and stability of the complexes toward oxidation waves explored by cyclic voltammetry are related to the electron withdrawing or releasing ability of the substituent of thiosemicarbazone moiety. The samples displayed Ni<sup>II</sup>/Ni<sup>I</sup> couples irreversible waves associated with Ni<sup>III</sup>/Ni<sup>II</sup> process.

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### 1. Introduction

Macrocyclic Schiff bases of thiosemicarbazones and their metal complexes are well known to be biologically important and interesting because of their anticarcinogenic, antibacterial, and antifungal properties [1,2]. Also, they have been screened for their medicinal properties because they posses some degree of cytotoxic activity [3].

The biological activity of certain thiosemicarbazones is due to their ability to form chelates with transition metal ions [4]. Crystal structures for salicylaldehyde thiosemicarbazone and 2-hydroxyacetophenone-thiosemicarbazone have been reported [5], and both mainly exist in the *E*-conformation with respect to the thiosemicarbazone azomethine bond. Biological activities may also related to the redox properties of the complexes [6]. The redox properties include oxidation and reduction of the central metal ion and various oxidation and reduction of the ligands, and the processes involve both the central atom and the ligand [6]. The redox potential of the Ni<sup>I</sup>/Ni<sup>II</sup> and Ni<sup>II</sup>/Ni<sup>III</sup> couples have been shown to be markedly affected by the nature of the solvent, background electrolyte, and the structure of the chelating ligand and the complex [7].

Ni(II) complexes of acetophenone, 4-aminoacetophenone, and 4-acetylacetophenone thiosemicarbazones containing the neutral or anionic forms of these ligands were prepared and fully characterized [8]. As a part of our work involving thiosemicarbazone derivatives and their complexes [9–11], this paper gives an insight about the preparation, spectral, characterization, and cyclic voltammetric studies of some Ni(II) complexes. The kinetics and thermodynamic parameters for some thermal decomposition steps as well as the mechanisms and kinetics of the electron transfer of the observed electrode couples for some complexes have been critically studied.

## 2. Experimental

All chemicals used were of analytical reagent grade (BDH) and used as supplied.

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Fig. 1. General formulas of the ligands.

## 2.1. Preparation of ligands

The thiosemcarbazone ligands (Fig. 1) were prepared by mixing equimolar amounts of acetopenone (12 ml, 0.1 mol), salicylaldehyde (12.2 ml, 0.1 mol), benzophenone (18.2 g, 0.1 mol), and/or *o*-hydroxymethoxybenzophenone (22.8 g, 0.1 mol) in 30 ml ethanol, with an ethanolic solution (20 ml) of thiosemicarbazide (9.1 g, 0.1 mol), ethyl- (11.9 g, 0.1 mol), phenyl- (16.7 g, 0.1 mol), and/or *p*-chlorophenyl (20.1 g, 0.1 mol) thiosemicarbazides. The reaction mixture were then refluxed on a water bath for 2-3 h. Few drops of glacial acetic acid being added at the onset of the reflux. The precipitates formed were separated out, filtered off, recrystallized from ethanol, and dried in a desiccator over anhydrous CaCl<sub>2</sub>. The proposed chemical structures of the prepared thiosemicarbazone ligands are in good agreement with the stoichiometries concluded from their analytical data and mass spectra (Table 1) and confirmed from the IR spectral data (Table 2). Most of these ligands are white or pale yellow and have melting point below 245 °C (Table 1).

The <sup>1</sup>H NMR spectra of the reagents HAET, HAPT, and H<sub>2</sub>HyMPT in d<sub>6</sub>-DMSO show signals at  $\delta = 12.08-11.40$  and 9.92–8.51 ppm assigned to the N<sup>2</sup>H and N<sup>4</sup>H protons, respectively [12]. The spectra of HAT and H<sub>2</sub>ST show signals at  $\delta = 10.29$ , 10.07, and 8.09, 8.03 ppm safely assigned to the NH<sub>2</sub> and NH protons, respectively. Moreover, the spectrum of H<sub>2</sub>ST shows the OH and NH<sub>2</sub> proton signals at 10.17 and 10.07 ppm [9], respectively. The general structure of the ligands is given in Fig. 1, where the abbreviations and their names are listed in Table 1.

Table 1

Abbreviation, name, melting point, elemental analysis and formula weight (F.W.) of the prepared ligands

Abbreviation	Name	m.p. (°C)	Found (Calcd.	%)	F.W.	
			С	Н	Found <sup>a</sup>	Calcd.
HAT	1-Acetophenonethiosemicarbazone	132	55.8 (55.9)	5.7 (5.7)	_	193.3
HAET	1-Acetophenone-4-ethylthiosemicarbazone	145	60.0 (59.7)	6.4 (6.8)	221.0	221.3
HAPT	1-Actophenone-4-phenylthiosemicarbazone	198	67.0 (66.9)	5.9 (5.6)	_	269.4
HApClPT	1-Acetophenone-4-p-chlorophenylthiosemicarbazone	190	58.8 (59.3)	4.2 (4.6)	304.0	303.8
$H_2ST$	1-Salicylaldehydethiosemicarbazone	245	49.3 (49.2)	5.0 (4.6)	-	195.2
H <sub>2</sub> SET	1-Salicylaldehyde-4-ethylthiosemicarbazone	184	53.3 (53.8)	5.4 (5.9)	223.0	223.3
$H_2SPT$	1-Salicylaldehyde-4-phenylthiosemicarbazone	205	61.0 (61.9)	4.8 (4.8)	_	271.3
$H_2SpClPT$	1-Salicylaldehyde-4-p-chlorophenylthiosemicarbazone	212	54.3 (54.9)	4.0 (3.9)	304.0	305.9
H <sub>2</sub> HyMBPT	1-(2-Hydroxy-4-methoxybenzophenone) 4-phenylthio-semicarbazone	110	66.0 (66.8)	4.8 (5.1)	377.0	377.5
H <sub>2</sub> HyMBpClPT	1-(2-Hydroxy-4-methoxybenzophenone) 4-p-chloro-phenylthiosemicarbazone	135	61.2 (61.2)	4.3 (4.4)	412.0	411.9
HBT	1-Benzophenonethiosimecarbazone	191	66.6 (65.8)	4.6 (5.1)	255.9	255.3

<sup>a</sup> Values obtained from mass spectra.

Table 2

Physical properties, analytical data and formula weight (F.W.) of the prepared nickel(II) complexes

No.	Complex	Color	m.p. (°C)	Found (Calcd	F.W.			
				С	Н	Ni	Found <sup>a</sup>	Calcd.
1	[Ni(AT) <sub>2</sub> ]H <sub>2</sub> O	Dark brown	268	47.5 (46.8)	4.4 (4.7)	12.3 (12.7)	_	461.1
2	[Ni(AET) <sub>2</sub> ]	Dark brown	234	52.3 (52.9)	5.1 (5.6)	11.4 (11.7)	499.0	499.3
3	[Ni <sub>2</sub> (APT) <sub>3</sub> (OH)(H <sub>2</sub> O)]H <sub>2</sub> O	Yellowish green	>300	55.0 (55.4)	4.0 (4.8)	11.9 (12.0)	_	975.5
4	$[Ni(ApClPT)_2]$	Yellowish brown	>300	54.8 (54.2)	4.2 (3.9)	8.6 (8.8)	664.0	664.3
5	[Ni(HST)(OAc)]	Pale brown	>300	38.1 (38.5)	3.5 (3.5)	19.2 (18.8)	312.0	311.9
6	$[Ni(SET)(H_2O)]1.5H_2O \cdot C_2H_5OH$	Reddish brown	>300	38.8 (38.8)	5.7 (5.9)	16.0 (15.8)	369.0	371.1
7	[Ni(HSPT)(OAc)(H <sub>2</sub> O) <sub>2</sub> ]	Brown	>300	44.9 (45.3)	4.5 (4.5)	13.8 (13.8)	422.0	424.1
8	[Ni(H <sub>2</sub> SpClPT)(OAc) <sub>2</sub> (H <sub>2</sub> O)]	Brown	>300	43.2 (43.0)	4.0 (4.3)	11.7 (11.3)	498.0	500.7
9	[Ni(HHyMBPT)(OH)(H <sub>2</sub> O)]	Yellow	223	53.0 (53.6)	3.9 (4.5)	12.5 (12.5)	470.0	470.2
10	[Ni <sub>2</sub> (H <sub>2</sub> HyMBpClPT)(Oac) <sub>4</sub> (H <sub>2</sub> O) <sub>3</sub> ]	Reddish brown	>300	42.1 (42.5)	4.4 (4.4)	14.1 (14.3)	820.0	819.5
11	[Ni(BT)(OAc)(H <sub>2</sub> O) <sub>2</sub> ]H <sub>2</sub> O	Greenish brown	>300	46.6 (47.1)	4.1 (4.7)	14.4 (14.4)	-	426.1

<sup>a</sup> Values obtained from mass spectra.

## 2.2. Preparation of complexes

All complexes were prepared by adding stoichiometric quantities of the ligands (3 mmol) in ethanol and nickel acetate (3 mmol) in bidistilled water. The reaction mixtures were then refluxed on a water bath for 4–6 h. The precipitates formed were filtered off, washed with hot water, hot ethanol, and diethylether, and finally dried in a vacuum desiccator over anhydrous CaCl<sub>2</sub>.

#### 2.3. Physical measurements

C and H content was determined at the Microanalytical Unit of Cairo University. The analysis of metal ions was carried out according to the standard methods [13].

The infrared spectra, as KBr discs, were recorded on a Mattson 5000 FTIR Spectrophotometer. The electronic and <sup>1</sup>H NMR (200 MHz) spectra were recorded on  $UV_{2-100}$  Unicam UV–Vis and a Varian Gemini Spectrophotometers, respectively. The mass spectra were recorded on a Varian MAT 311 instrument. The thermal studies were carried out on a Shimadzu thermogravimetric analyzer at a heating rate of 10 °C min<sup>-1</sup>. The cyclic voltammetry measurements were carried out with a Potentiostat wave generator (Oxford Press) equipped with a Phillips PM 8043 X-Y recorder. The electrode assembly consists of platinum wires of 0.5 diameter as working and counter electrodes and Ag/AgCl as a reference electrode. Tetrabutylammonium tetraflouroborate (TBA<sup>+</sup>BF<sub>4</sub><sup>-</sup>) was used as supporting electrolyte.

#### 3. Results and discussion

The isolated complexes are stable in air, insoluble in water and common organic solvents, but completely soluble in DMF and DMSO except for  $[Ni(AT)_2]H_2O$ ,  $[Ni(HHyMBPT)(OH)(H_2O)]$ ,  $[Ni(AET)_2]$ , and  $[Ni_2(H_2$  $HyMBpClPT)(OAc)_4(H_2O)_3]$ , which are partially soluble in DMF and DMSO. The elemental analysis, color, and melting point together with the formula weight obtained from the ms spectra for the complexes are listed in Table 2. Attempts to propose the structure of the isolated complexes come from full investigation using the following studies.

### 3.1. IR spectral studies

The most characteristic bands of the ligands and their complexes are summarized in Table 3. Representative example for their spectra is given in Fig. 2.

The coordination sites of ligands under investigation with Ni(II) ions were elucidated using IR spectra. The data obtained suggest that the ligands bind to the metal ions by several manners. Firstly, HAT, HAET, HAPT, HApClPT, and HBT behave as mononegative bidentate and coordinate through the C=N and C-S groups with displacement of one hydrogen atom upon enethiolization. The mode of coordination was found in [Ni(AT)<sub>2</sub>]H<sub>2</sub>O, [Ni(AET)<sub>2</sub>], [Ni<sub>2</sub>(APT)<sub>3</sub>(OH)(H<sub>2</sub>O)]H<sub>2</sub>O, [Ni(ApClPT)<sub>2</sub>], and [Ni(BT)(OAc)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O, and was suggested by the following evidence: (i) the disappearance of  $\nu(N^2H)$ , (ii) the shift of  $\nu$ (C=N) to lower frequency by 10–65 cm<sup>-1</sup> [14], (iii) the appearance of a new band attributed to  $\nu$ (C=N<sup>\*</sup>) at the same spectral region for the  $\nu$ (C=N) of the thiosemicarbazone moiety, (iv) coordination of the azomethine nitrogen is also consistent with the presence of a new band at 440–460 cm<sup>-1</sup> assignable to the  $\nu$ (Ni–N) vibration [15], and (v) the thioamide band (IV) is absent with the simultaneous appearance of new bands in the 610-680 and  $345-370 \text{ cm}^{-1}$  regions due to the  $\nu(C-S)$  [16] and  $\nu(Ni-S)$ vibrations [17], respectively.

Secondly, H<sub>2</sub>SpClPT and H<sub>2</sub>HyMBpClPT appear to be in the thioketo form, neutral, and tridentate, coordinating via the C=S, C=N, and phenolic oxygen groups. This behavior is observed in [Ni(H<sub>2</sub>SpClPT)(OAc)<sub>2</sub>(H<sub>2</sub>O)] and [Ni<sub>2</sub>(H<sub>2</sub>HyMBpClPT)(OAc)<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>] and supported by the following evidence: (i) the  $\nu$ (C=S) and  $\nu$ (C=N) bands are shifted to lower frequency by 5–45 cm<sup>-1</sup>, and (ii) the

Table 3

Significant IR spectral bands (cm<sup>-1</sup>) of the nickel(II) complexes with relevant bands of the free ligand in parenthesis

Complex	$\nu(NH_2)$	ν(OH)	$\nu(N^4H)$	$\nu(N^2H)$	ν(C=N)	ν(C=S)	v(C-S)	$\delta(OH)$	v(Ni–O)	v(Ni–N)	v(Ni-S)
1	3395 (3410) 3345 (3370)	_	_	(3220)	1620 (1630)	(790)	645	_	_	454	355
2	-	_	3210(3320)	(3225)	1565 (1630)	(790)	610	_	_	445	365
3	_	3435	3290(3300)	(3250)	1575 (1605)	(795)	615	1340	_	460	345
4	_	_	3280(3290)	(3240)	1590 (1635)	(795)	610	_	_	450	370
5	3325 (3370)	3405 (3440)	-	(3165)	1605 (1610)	(780)	650	1330 (1365)	505	425	350
	3260 (3315)										
6	-	(3405)	3330 (3355)	(3250)	1595 (1605)	(790)	620	1330 (1375)	500	440	340
7	_	3420 (3405)	3385 (3380)	(3145)	1600 (1620)	(835)	655	1375 (1389)	500	450	350
8	_	3320 (3335)	3230 (3235)	3130 (3154)	1605 (1610)	820 (830)	_	1305(1330)	505	420	345
9	_	3460 (3470)	3295 (3300)	3160 (3160)	1590 (1635)	810 (810)	_	1320(1327)	505	440	_
10	_	3430 (3440)	3230 (3290)	3110 (3180)	1590(1635)	745 (790)	_	1310(1350)	505	410	385
11	3365 (3365)	-	-	(3175)	1590 (1620)	(800)	680	-	490	440	355



Fig. 2. IR spectra of: (a) [Ni<sub>2</sub>(H<sub>2</sub>HyMBpClPT)(OAc)<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>] and (b) [Ni(BT)(OAc)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O.

phenolic oxygen of these ligands occupy the third coordination site with the shift of  $\nu$ (OH) band by 10–15 cm<sup>-1</sup> to lower frequency. The band at 505 cm<sup>-1</sup> is assignable to  $\nu$ (Ni–O) of the bridging phenolate oxygen, and (iii) the appearance of new bands in the low frequency region at 345–385 and 410–420 cm<sup>-1</sup>, which are assigned to the  $\nu$ (Ni–S) and (Ni–N) [18] vibrations, respectively.

The third mode of chelathion was found through the C=N, C–S, and phenolic oxygen groups in which H<sub>2</sub>ST and H<sub>2</sub>SPT act as mononegative tridentates. This behavior is found in [Ni(HST)(OAc)] and [Ni(HSPT)(OAc)(H<sub>2</sub>O)<sub>2</sub>]. Elucidation of this mode is proposed by: (i) the disappearance of  $\nu$ (N<sup>2</sup>H), (ii) the shift of  $\nu$ (C=N) bands to lower frequency by 50–20 cm<sup>-1</sup>, (iii) the disappearance of  $\nu$ (C=S) with the appearance of a new band at 650–655 cm<sup>-1</sup>, (iv) the shift (15–35 cm<sup>-1</sup>) of  $\nu$ (OH) and (15–35 cm<sup>-1</sup>) of  $\delta$ (OH) to lower frequency, and (v) new bands appeared in the low frequency region for  $\nu$ (Ni–S) at 350 cm<sup>-1</sup>,  $\nu$ (Ni–N) at 425–450 cm<sup>-1</sup>, and  $\nu$ (Ni-O) at 500–505 cm<sup>-1</sup> gave a good evidence for the participation of S, N, and O donors.

In [Ni(SET)(H<sub>2</sub>O)]1.5H<sub>2</sub>O·C<sub>2</sub>H<sub>5</sub>OH, the ligand releases the hydrogen ions from both the thioketo, through thioenolization, and the OH groups and behaves as a binegative tridentate. This behavior was confirmed based on the following evidence: (i) the disappearance of  $\nu$ (N<sup>2</sup>H) and  $\nu$ (C=S) conjugated with the appearance of  $\nu$ (C–S) at 620 cm<sup>-1</sup> and  $\nu$ (Ni-S) at 340 cm<sup>-1</sup>, (ii) the deprotonated OH group occupies the third (through bridging) coordination site, (iii) the shift of  $\nu$ (C=N) band from 1605 to 1595 cm<sup>-1</sup>, and (iv) the new bands observed at 440 and 500 cm<sup>-1</sup> attributed to the  $\nu$ (Ni–N) and  $\nu$ (Ni–O) vibrations, respectively, gave a good evidence for the participation of N and O donors.

In [Ni(HHyMBPT)(OH)(H<sub>2</sub>O)], H<sub>2</sub>HyMBPT behaves as a mononegative, bidentate ligand coordinating via the deprotonated OH and C=N groups as shown in Scheme 1. The mode of complexation is suggested by the clear change in the position of  $\nu$ (C=N) band by 44 cm<sup>-1</sup>, the shift of  $\nu$ (OH) and  $\delta$ (OH) to lower frequency, the appearance of new bands at 440 and 505 cm<sup>-1</sup> assigned to  $\nu$ (Ni–N) and  $\nu$ (Ni–O). Also, the  $\nu$ (C=S) and  $\nu$ (N<sup>2</sup>H) bands remain unshifted, suggesting that the C=S group is out of coordination.

The acetate group coordinates in a monodentate or bidentate manner [19]. The monodentate in [Ni(HST)(OAc)], [Ni (HSPT)(OAc)(H<sub>2</sub>O)<sub>2</sub>], and [Ni(H<sub>2</sub>SpClPT)(OAc)<sub>2</sub>(H<sub>2</sub>O)] is



Scheme 1.

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deduced from the frequency difference  $(\Delta \nu)$  between  $\nu_s$  and  $\nu_{as}$  (more than 185 cm<sup>-1</sup>) [20]. The bidentate behavior of the acetate group in [Ni(BT)(OAc)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O is supported by the appearance of two new bands at 1420 and 1525 cm<sup>-1</sup> due to symmetric and asymmetric stretching vibrations, respectively. [Ni<sub>2</sub>(H<sub>2</sub>HyMB*p*ClPT)(OAc)<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>] displays three bands in its spectrum at 1525, 1395, and 1337 cm<sup>-1</sup>, which are assigned to the existence of bidentate and monodentate coordinations of the acetate group [21]. The monodentate behavior is deduced from the frequency difference ( $\Delta \nu = 188 \text{ cm}^{-1}$ ) between the 1525 and 1337 cm<sup>-1</sup> bands, and the difference between the 1525 and 1395 cm<sup>-1</sup> ( $\Delta \nu = 88 \text{ cm}^{-1}$ ) bands is correlated to the bidentate behavior.

#### 3.2. Magnetic and electronic spectral studies

The magnetic moments and electronic spectral bands of the complexes are summarized in Table 4.

The magnetic moment values of  $[Ni(HSPT)(OAc)(H_2 O)_2]$ ,  $[Ni(H_2SpClPT)(OAc)_2(H_2O)]$ ,  $[Ni_2(H_2HyMBpClPT)(OAc)_4(H_2O)_3]$ , and  $[Ni(BT)(OAc)(H_2O)_2]H_2O$  are found within the range reported for the octahedral geometry around the Ni(II) ion [22]. The value (1.8 B.M.) measured for each nickel atom in  $[Ni_2(H_2HyMBpClPT)(OAc)_4(H_2O)_3]$  is less than that reported for systems containing two unpaired electrons, which may be attributed to the existence of nickel–nickel interaction [23].

The electronic spectra of these complexes, recorded in Nujol mull and DMF solutions, have a great similarity and show two main broad bands centered at 16,665-18,050 and  $23,255-24,510 \text{ cm}^{-1}$  assigning to the  ${}^{3}\text{A}_{2g} \rightarrow {}^{3}\text{T}_{1g}$  (F) and  ${}^{3}\text{A}_{2g} \rightarrow {}^{3}\text{T}_{1g}$  (P) transitions, respectively, in an octahedral geometry [24]. The proposed structures for [Ni(HSPT)(OAc)(H<sub>2</sub>O)<sub>2</sub>], [Ni(BT)(OAc)(H<sub>2</sub>O)<sub>2</sub>]H<sub>2</sub>O, and [Ni<sub>2</sub>(H<sub>2</sub>HyMB*p*ClPT)(OAc)<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>] are shown in Scheme 2 (a, b, and c, respectively). The spectrochemical



parameters Dq, *B*, and  $\beta$  of some of the complexes are given in Table 4. The Dq values are found in the range  $(9.80-10.3) \times 10^3 \text{ cm}^{-1}$  close to that observed for NiO<sub>4</sub>N<sub>2</sub> and reasonable for most complexes containing oxygen, nitrogen, and/or sulphur. The observed Dq values ordered the ligands in the middle range of the spectrochemical series and provides that the C=N, OH, and C=S of the ligands are complexed to the Ni(II) ion in an octahedral geometry.

The *B* values of the prepared octahedral complexes (Table 4) were found in the range 69.9–72.0% that of the free ion ( $B^{\circ} = 1030 \text{ cm}^{-1}$ ) [25], indicating considerable overlap with strongly covalent nickel-ligand bond character [23]. The decrease in *B* values is most likely associated with the reduction in the nuclear charge of the cation.

Table 4

Magnetic moment, electronic spectral data in DMF and nujol (in parentheses) of the nickel(II) complexes with some ligand field parameters

Complex	$\mu_{ m eff}$	$v_{\rm max}~({\rm cm}^{-1})$	Ligand field p	Supposed structure		
	(B.M.)		$B (\mathrm{cm}^{-1})$	$B \text{ (cm}^{-1}) \qquad \beta$		
1	0.90	22575 (20875), 18380 (17575)	_	_	_	Tetrahedral + square planar (nujol)
2	3.51	16865 (17300)	_	_	-	Tetrahedral
3	3.21	24690, 17950 (17390)	_	_	-	Tetrahedral
4	2.16	24570 (20705), 16665 (17855)	_	_	-	Tetrahedral + square
						planar (nujol)
5	0.95	24440 (20240), 17390 (17665)	_	_	-	Tetrahedral + square
						planar (nujol)
6	1.26	20245 (20450), 16475 (17210)	_	_	-	Tetrahedral + square
						planar
7	3.05	23925 (23925), 17545 (18050)	750 (7640)	0.72 (0.74)	100060 (10170)	Octahedral
8	2.80	23585 (23585), 16950 (17730)	720 (750)	0.66 (0.72)	9900 (10000)	Octahedral
9	3.80	17450 (17270)	_	_	_	Tetrahedral
10	1.80	23925 (23255), 17240 (17220)	700 (730)	0.68 (0.71)	10395 (9830)	Octahedral
11	2.90	23420 (24510), 17360 (16665)	740 (710)	0.71(0.68)	9905 (10180)	Octahedral

The nephelauxetic parameter,  $\beta$  is in the range 0.66–0.74, indicating that these ligands are in the middle of the nephelauxetic of other nitrogen, sulphur, and oxygen donor series. The values are higher than that observed for NiN<sub>6</sub> or NiO<sub>6</sub>, confirming the coordination via N, O, and/or S. Thus, it seems reasonable to presume that most of the chelates formed in this series involve NiO<sub>4</sub>NS or NiO<sub>4</sub>N<sub>2</sub> chromophores.

The magnetic moment values (3.51, 3.21, and 3.80 B.M.) measured for the complexes [Ni(AET)<sub>2</sub>], [Ni<sub>2</sub>(APT)<sub>3</sub>(OH)-(H<sub>2</sub>O)]H<sub>2</sub>O, and [Ni(HHyMBPT)(OH)(H<sub>2</sub>O)] lie in the range reported for a tetrahedral structure [26]. The lower value measured per one nickel atom for the binuclear complex may be due to nickel–nickel interaction [23]. This geometry is further evidenced by the electronic spectral data, which show one d–d transition band at 16,865–17,950 cm<sup>-1</sup>, which is assigned to the  ${}^{3}T_{1} \rightarrow {}^{3}T_{1}$  (P) transition.

The complexes [Ni(AT)<sub>2</sub>]H<sub>2</sub>O, [Ni(ApClPT)<sub>2</sub>], [Ni(HST) (OAc)], and  $[Ni(SET)(H_2O)]1.5H_2O \cdot C_2H_5OH$  have 0.90, 2.16, 0.95, and 1.26 B.M. magnetic moments, respectively, which are less than that reported for the d<sup>8</sup>-octahedral and/or tetrahedral complexes and higher than diamagnetic square-planar complexes. The values may suggest the existence of the complexes in a mixed stereochemistry [27]. Such supposition is also confirmed from the analysis of their electronic spectra, which show two bands. The band observed at  $16,475-18,380 \text{ cm}^{-1}$  is in accordance with a tetrahedral configuration and assigned to the  ${}^{3}T_{1} \rightarrow {}^{3}T_{1}$  (P) d-d transition. The other band at  $20,240-22,575 \text{ cm}^{-1}$  is referring to a square-planar geometry [11]. The DMF has a large effect in the spectra of  $[Ni(ApClPT)_2]$ ,  $[Ni(AT)_2]H_2O$ , and [Ni(HST)(OAc)] and no effect in the spectrum of  $[Ni(SET)(H_2O)]$ 1.5H<sub>2</sub>O · C<sub>2</sub>H<sub>5</sub>OH, indicating that the DMF acts as a ligand in such complexes. Scheme 3 (a-c) represents the structure of [Ni(AT)<sub>2</sub>]H<sub>2</sub>O, [Ni(AET)<sub>2</sub>], and [Ni(ApClPT)<sub>2</sub>], respectively.

The spectra and the position of the bands of some complexes in DMF are found to be different from the corresponding ones recorded in nujol (Table 4), showing that these complexes are significantly unstable, commencement of solvolysis or presence of low symmetry components of crystal field [23]. These complexes could also undergo chemical dissolution in DMF and hence the composition of the chromophores may become different in solution than in solid.





Fig. 3. Mass spectrum of the complex [Ni(HST)(OAc)].

#### 3.3. Mass spectra

The mass spectra of most complexes were recorded and their molecular ion peaks confirm the suggested formula of these complexes. The calculated and found values of the molecular weights of some of the complexes are given in Table 2. Representative mass spectrum of the complex [Ni(HST)(OAc)] is shown in Fig. 3. The spectrum shows numerous peaks representing successive degradation of the molecule. The observed peak at m/e 312.0 (Calcd. 311.7) represents the molecular ion peak of the complex with 30.19% abundance. Scheme 4 demonstrates the proposed paths of the decomposition steps for the investigated complex. One of the strongest peaks (base peak) at m/e 91.0 represents the stable species C<sub>2</sub>H<sub>5</sub>NOS.

#### 3.4. Thermal studies

#### 3.4.1. Kinetic analysis

Non-isothermal kinetic analyses for the decomposition of HAET, HAPT, and H<sub>2</sub>HyMBPT and some Ni(II) complexes were carried out by the application of two different procedures: the Coats-Redfern [28] and the Horowitz-Metzger [29] methods. The kinetic parameters (*E* and *n*) were calculated according to the above two methods, where the thermodynamic parameters ( $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$ ) were calculated according to the Coats-Redfern equation and their values are tabulated in Table 5. The activation enthalpy ( $\Delta H^*$ ), the activation entropy ( $\Delta S^*$ ), and the free energy of activation



Scheme 4. Proposed fragmentation pattern of [Ni(HST)(OAc)].

 $(\Delta G^*)$  were calculated using the following equations:

$$\Delta S^* = 2.303 \left[ \log \left( \frac{Zh}{KT} \right) \right] R$$
$$\Delta H^* = E - RT$$
$$\Delta G^* = \Delta H^* - T_s \Delta S^*$$

where Z, K, and h are the pre-exponential factor, Boltzman, and Plank constants, respectively [30]. Comparison of the two sets of kinetic parameters shows no significant difference between them considering the approximations



Scheme 5. Proposed thermal decomposition pattern of [Ni(AET)2].

involved in the Horowitz-Metzger method. The activation energies could not be calculated for the overlapping or unsuitable steps. The relatively high *E* values indicate that the ligand is strongly bonded to the Ni(II) ions. The negative  $\Delta S^*$  values in [Ni<sub>2</sub>(APT)<sub>3</sub>(OH)(H<sub>2</sub>O)]H<sub>2</sub>O (third step) and [Ni<sub>2</sub>(H<sub>2</sub>HyMB*p*CIPT)–(OAc)<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>] (first and second steps) indicate that the activated complexes have more ordered structure than the reactants and the reactants are slower than the normal [30,31].

The thermal decomposition of some ligands and complexes was recorded at temperature 30-1000 °C. The thermograms exhibit several thermal events. The first step in the TG thermogram of some complexes corresponds to the expulsion of water of crystallization and/or coordination. The end products for most complexes were NiS or NiO. The activation energies calculated for the first step in the TG thermograms of the ligands and complexes lie in the ranges 83.9-127.7 and 164.0-304.0 kJ mol<sup>-1</sup>, respectively (Coats-Redfern equation).

The thermal decomposition of  $[Ni(AET)_2]$  (Fig. 4) as an example for the decomposition of these compounds shows three steps at 220–312, 459–551, and 553–660 °C (Scheme 5). The first step due to elimination of  $2(C_{10}H_{13}N)$ 

Table 5

Kinetic parameters of the thermal decomposition of some of ligands and their complexes<sup>a</sup>

Compound	Step	Coats-Redfern equation			Horowitz-Metzger equation			$\Delta S^*$	$\Delta H^*$	$\Delta G^*$
		r	n	E	r	n	E			
HAET	1st	0.9989	1.00	100.9	0.9980	1.00	107.1	-141.8	96.7	167.4
НАРТ	1st	0.9999	0.66	83.9	0.9998	0.66	89.6	-164.1	79.9	158.9
H <sub>2</sub> HyMBPT	1st	0.9982	2.00	127.7	0.9973	2.00	138.3	-58.8	123.8	151.1
	2nd	0.9987	2.00	140.1	0.9977	2.00	145.7	-88.4	135.4	185.6
[Ni(AET) <sub>2</sub> ]	1st	1.0000	2.00	296.2	1.0000	2.00	309.5	119.6	232.4	170.3
[Ni <sub>2</sub> (APT) <sub>3</sub> (OH)(H <sub>2</sub> O)]H <sub>2</sub> O	3rd	0.9922	0.33	183.6	0.9940	0.33	191.3	-25.2	179.1	193.8
	6th	0.9995	1.00	284.5	0.9995	1.00	295.3	2.4	253.0	276.0
[Ni(ApClPT) <sub>2</sub> ]	1st	0.9707	1.00	304.2	0.9707	1.00	311.2	255.7	299.7	166.9
[Ni(HhyMBPT)(OH)(H <sub>2</sub> O)]	2nd	0.9962	1.00	304.7	0.9958	1.00	315.1	178.2	299.8	196.1
[Ni <sub>2</sub> (H <sub>2</sub> HyMB <i>p</i> ClPT)(Oac) <sub>4</sub> (H <sub>2</sub> O) <sub>3</sub> ]	1st	0.9993	1.00	164.0	0.9992	1.00	173.4	-25.1	159.7	146.6
	2nd	0.9999	1.00	46.5	0.9985	1.00	60.5	-299.1	70.1	252.5

<sup>a</sup>  $r = \text{correlation coefficient}, n = \text{order of the decomposition reaction}; E, \Delta H^*$ , and  $\Delta G^*$  are in kJ mol<sup>-1</sup>,  $\Delta S^*$  in J K mol<sup>-1</sup>.



Fig. 4. TG (A) and DTG (B) thermograms of the complex [Ni(AET)<sub>2</sub>].

Table 6									
Electrochemical	data of	some of	f the	prepared	nickel(II)	complexes	in I	OMF-TBA+	$BF_4^a$

Complex	First electr	ode couple			Second electrode couple				
	E <sub>p,a</sub>	Ep,c	$\Delta E_{\rm p}$	$E_{1/2}$	$E_{\rm p,a}$	E <sub>p,c</sub>	$\Delta E_{\rm p}$	$E_{1/2}$	
[Ni(AT) <sub>2</sub> ]H <sub>2</sub> O	-1.12	-1.39	0.27	-1.25	1.28	0.94	0.34	1.11	
[Ni(AET) <sub>2</sub> ]	-0.80	-1.20	0.40	-1.00	1.19	1.14	0.05	1.16	
[Ni <sub>2</sub> (APT) <sub>3</sub> (OH)(H <sub>2</sub> O)]H <sub>2</sub> O	-0.20	-0.78	0.58	-0.49	0.86	0.78	0.08	0.82	
[Ni(ApClPT) <sub>2</sub> ]	-0.72	-1.08	0.36	-0.90	1.20	0.98	0.22	1.09	

<sup>a</sup> Scan rate =  $100 \text{ mV sec}^{-1}$ ;  $E_{1/2} = (E_{p,c} + E_{p,a})/2$ .

(Calcd. 58.9%, found 58.9%) has activation energy of  $296.2 \text{ kJ mol}^{-1}$  and second order reaction. Elimination of 2NH (Calcd. 6.0%, found 7.0%) takes place in the second step. The second and third steps are not suitable for kinetic analysis. The final stable residue as identified from the mass loss consideration is NiS (Calcd. 18.1%, found 17.7%).

#### 3.5. Cyclic voltammetry

The cyclic voltammetric behavior of the complexes  $[Ni(AT)_2]H_2O$ ,  $[Ni(AET)_2]$ ,  $[Ni_2(APT)_3(OH)(H_2O)]H_2O$ , and  $[Ni(ApCIPT)_2]$  in DMF–TBA<sup>+</sup>BF4<sup>-</sup> are found similar and displayed two well-defined electrode couples. The results are summarized in Table 6. Representative data are also shown in Fig. 5. The complexes showed two successive one electron processes. The first electrode couple of these complexes is safely assigned to the irreversible couple Ni<sup>II</sup>/Ni<sup>I</sup> with  $E_{1/2}$  of -0.49 to -1.25 V ( $\Delta E_p = 0.27-0.58$  V) and represented as follows:



Fig. 5. Cyclic voltammogram of the complex  $[Ni(AT)_2]H_2O$  in  $DMF-TBA^+BF^-{}_4$  vs. Ag/AgCl electrode.



Fig. 6. The dependence of the cathodic peak potential  $E_{p,c}$  (A) and the cathodic peak current  $i_{p,c}$  (B) of the electrode couple Ni<sup>II</sup>/Ni<sup>I</sup> of the complex [Ni(AT)<sub>2</sub>]H<sub>2</sub>O.

 $Ni^{II}L + e^- \leftrightarrow Ni^IL$ 

The second electrode couple wit  $E_{1/2} = 0.82 - 1.11 \text{ V}$  is assigned to the irreversible electrode couple Ni<sup>II</sup>/Ni<sup>III</sup> by comparison with analogous Ni(II) complexes [7]. The irreversible nature of the observed electrode couples has been established by comparing its peak current height  $(I_{p,c}/I_{p,a})$ 1) with other similar complexes [7]. The irreversible nature of this couple is also confirmed by the linear dependence of the cathodic peak potential  $(E_{p,c})$  with logaritm sweep rate  $(\log v)$  as shown in Fig. 6A. From the slope of this line and assuming the number of electrons (n) involved in the oxidation step equals one, the value of the electron transfer coefficient ( $\alpha$ ) is 0.59. The peak-to-peak potential separation  $(\Delta E_p)$  of the electrode couple Ni<sup>II</sup>/Ni<sup>III</sup> increased with increasing the scan rate confirming the occurrence of a slow chemical reaction and a limited mass transfer following the electrode process [32]. Thus, the electron transfer process is irreversible and the species that initially formed in the electrode process may also react further to give products that are not reoxidezed at the same potintial as in the first formed species [33].

The dependence of the voltammetric responses of the Ni<sup>II</sup>/Ni<sup>III</sup> couple on the scan rate and on the depolarizer concentration is that typical of an ECE (chemical reaction coupled between two charge transfer processes) mechanism in which an irreversible first order chemical reaction is interposed between two successive one-electron transfers [34]. For an ECE process with an irreversible chemical reaction,  $i_{\rm p,c}/v^{1/2}$  showed decrease with increasing scan rate. The ratio  $i_{\rm p,c}/v^{1/2}$  slowly decreases with scan rate (20–200 mV/sec) for all complexes, confirming that the observed behavior favors the ECE mechanism. The dependence of the cathodic peak current  $i_{\rm p,c}$  of the electrode couple Ni<sup>II</sup>/Ni<sup>III</sup> on the square rate of the sweep rate ( $v^{1/2}$ ) suggests diffusion-controlled electrochemical process (Fig. 6B).

As may be observed in Table 6, substitution on thiosemicarbazone moiety has a significant effect on  $E_{1/2}$  for the complexes; electron-withdrawing groups stabilize the Ni(II) in the complexes [Ni<sub>2</sub>(APT)<sub>3</sub>(OH)(H<sub>2</sub>O)]H<sub>2</sub>O and [Ni(ApClPT)<sub>2</sub>] while the electron-donating group favor oxidation to Ni(III). This is possibly because the electron-withdrawing chlorine or phenyl ring makes the complex more positively charged and hence causes it to be more easily reduced. Similarly the electron-donating groups make the complexes [Ni(AT)<sub>2</sub>]H<sub>2</sub>O and [Ni(AET)<sub>2</sub>] less positively charged and hence less easily reduced. The oxidation potential of this couple does not correlate linearly with the Hummett constant ( $\sigma$ ), and the  $E^{\circ}$  of the couple is sensitive to the nature of the substituent in the thiosemicarbazone moiety with Ni<sup>II</sup>/Ni<sup>III</sup>.

#### 4. Conclusion

A series of Ni(II) complexes of some thiosemicarbzones have been prepared and fully characterized. The kinetic and thermodynamic characteristics of some of the prepared complexes are discussed. Proposed fragmentation and thermal decomposition patterns for some of the complexes are also given. The cyclic voltammetric of the complexes showed that the Ni(II) compounds undergo one-electron reduction and oxidation to form the corresponding Ni(I) and Ni(III) compounds. The Ni(I) and Ni(III) compounds may be found being used as one-electron redox reagents since the former is a strong reducing agent and the latter is strong oxidizing agent.

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