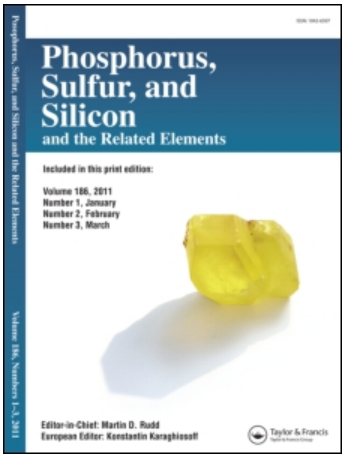

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Mixed Ligand Complexes of Nickel (II) Dialkyldithiophosphates with 2-Acetylpyridine Semicarbazone and 2-Acetylpyridine Benzoylhydrazone

Amna S. A. Zidan[a]
[a] Assiut University, Assiut, Egypt

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DOI: 10.1080/1042650039017023

MIXED LIGAND COMPLEXES OF NICKEL (II) DIALKYLDITHIOPHOSPHATES WITH 2-ACETYLPYRIDINE SEMICARBAZONE AND 2-ACETYLPYRIDINE BENZOYLHYDRAZONE

Amna S. A. Zidan
Assiut University, Assiut, Egypt

(Received May 10, 2002; accepted August 12, 2002)

Dialkyldithiophosphates nickel (II) complexes react with Apsc and HApBH to yield mixed ligand complexes of the types [Ni{$(RO)_2PS_2$}$_2$(Apsc)] and [Ni{$(RO)_2PS_2$}(ApBH)] where R = methyl, ethyl, or propyl; Apsc = 2-Acetylpyridine semicarbazone; HApBH = 2-Acetylpyridine benzoylhydrazone. From the elemental analysis and UV, IR, and mass spectra the composition and structures of the complexes and the ligand (HApBH) were determined. TG and DTG techniques were used to investigate the thermal behavior of HApBH and the complexes. The IR spectra show that Apsc acts in a neutral bidentate fashion and HApBH behaves in all cases as a mononegative tridentate ligand. The electronic spectral data suggest an octahedral structure of these complexes. Also the biological activity for some of the complexes and HApBH was recorded against some bacteria and fungi. The HApBH ligand has a high toxicity against bacteria and fungi under study; this may be due to presence of the pyridyl ring and hydroxyl group of the compound.

Keywords: 2-Acetylpyridine benzoylhydrazone; 2-acetylpyridine semicarbazone; mixed ligand complexes; nickel (II) dialkyldithiophosphates; spectroscopic characterization; thermal analysis

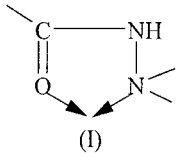
INTRODUCTION

Semicarbazones and hydrazones are very biologically active and most importantly, nitrogen/oxygen donor ligands. The activity increases on complexation with metal ions.[1–5] The real impetus for developing the coordination chemistry of these potential ligands was probably

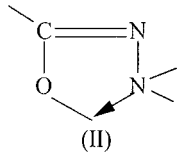
Address correspondence to Amna S. A. Zidan, Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt. E-mail: amna@aun.edu.eg

provided by the remarkable antiviral,[6] antimalarial, and antituberculosis effects.[7–9] The antituberculous activity of hydrazides was described for their ability to form more or less stable chelates with the transition metal ions.[10]

The reaction of arylhydrazones with transition metal ions can proceed according to two pathways attaining the ketonic (I) or enolic (II) structure for the hydrazide part of the molecule.

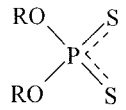


(I) Ketonic form

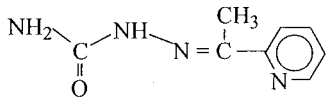


(II) Enolic form

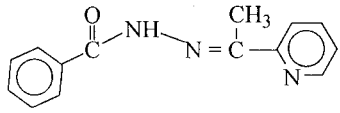
The mode of bonding was found to depend on the nature of both the ligand and metal ions.[11,12]



R= methyl, ethyl or propyl of dithiophosphate



Apsc=2-acetylpyridine semicarbazone



HApBH=2-acetylpyridine benzoylhydrazone

Moreover, the dialkyldithiophosphates are biologically important[13] and later used as antioxidant on vegetable oil for lubricant application.[14] In continuation of our previous studies on mixed ligand complexes of nickel (II) dialkyldithiophosphates with nitrogen donor ligands,[15] we describe here the synthesis, spectral and thermal analyses, and mass spectra of some mixed ligand complexes of 2-acetylpyridine semicarbazone and 2-acetylpyridine benzoylhydrazone with bis (dialkyldithiophosphato) Ni(II).

EXPERIMENTAL

All chemicals were of analytical grade; hydrazine hydrate, 2-acetylpyridine, and semicarbazide hydrochloride were Merck grade. They were used without further purification.

Bis (dialkyldithiophosphato) nickel (II),[16] benzoylhydrazine,[17] and 2-acetylpyridine semicarbazone[5] were prepared according to literature methods.

PHYSICAL MEASUREMENTS

The elemental analysis data were obtained by Analytischer Funktionstest vario EL Fab-Nr. 11982027 apparatus. The infrared spectra were recorded on a 470 Shimadzu infrared spectrophotometer. The electronic absorption spectra measurements were carried out on an UV-2101 PC Shimadzu spectrophotometer. JEOL-JMS600 apparatus recorded the mass spectra. The thermogravimetric analyses were determined using an electrobalance of the type sartorius 200 MP converted to a thermobalance by the addition of a small furnace and sample holder. The temperature was measured using a Chromal-Alumal thermocouple attached to a digital multimeter type Soar ME-550, the heating rate was adjusted to be $8^{\circ}C\ min^{-1}$.

Preparation of 2-Acetylpyridine Benzoylhydrazone (HApBH)

The ligand was prepared by refluxing equimolar mixtures of 12.10 g 2-acetylpyridine (0.2 mmol) and 12.00 g benzoylhydrazine (0.2 mmol) in 50 ml absolute ethanol on a water bath for 8 h. After cooling the reaction mixture, white crystals were isolated. The product was filtered off and washed with ethyl alcohol, recrystallized from absolute ethanol, and finally dried in a desiccator over anhydrous calcium chloride (yield 70% m.p 165°).

Preparation of the Complexes

The mixed ligand complexes were prepared by adding 0.1 mmol of 2-acetylpyridine semicarbazone (0.36 g) or 0.48 g of 2-acetylpyridine benzoylhydrazone in 20 ml hot ethanol to a solution of 0.1 mmol of bis (dialkyldithiophosphato) nickel (II) (0.74 g of dimethyldithiophosphato Ni(II), 0.85 g of diethyldithiophosphato Ni(II) and 0.96 g of dipropyldithiophosphato Ni(II)) in 20 ml hot chloroform with continuous stirring. The color of the mixture becomes green or yellowish green.

The solid crystals were separated after three days, filtered and washed with diethyl ether several times, and dried over calcium chloride.

RESULTS AND DISCUSSION

The complexes are partially soluble in ethanol and common organic solvents; they have good solubility in DMF and DMSO. Analytical data, color, and melting or decomposition points are tabulated in Table I. The mixed ligand complexes are formed according to the following equations:

$$[Ni\{(RO)_2PS_2\}_2] + Apsc \rightarrow [Ni\{(RO)_2PS_2\}_2(Apsc)] \quad (1)$$

$$[\{Ni(RO)_2PS_2\}_2] + HApBH \rightarrow [Ni\{(RO)_2PS_2\}(ApBH).] + (RO)_2PS_2H \quad (2)$$

Where

$$R = CH_3, C_2H_5, \text{ or } n\text{-}C_3H_7\text{-dithiophosphate.}$$

IR Spectra

The main spectral bands of the ligand 2-acetylpyridine benzoylhydrazone (HApBH) and the prepared complexes are listed in Table II.

TABLE I Analytical Data and Physical Properties of HApBH and the Complexes

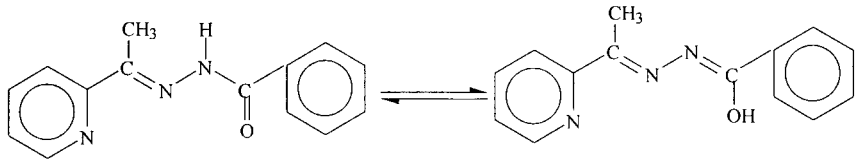
No.	Complex	Color	C% (calc.)	H% (calc.)	N% (calc.)	S% (calc.)	Dec. P.C°
1	$[Ni\{(MeO)_2PS_2\}_2(Apsc)]$	Green	26.20 (26.15)	4.00 (4.02)	10.17 (10.16)	23.30 (23.27)	180
2	$[Ni\{(EtO)_2PS_2\}_2(Apsc)]$	Green	31.70 (31.64)	4.95 (4.98)	9.25 (9.23)	21.15 (21.12)	210
3	$[Ni\{(PrO)_2PS_2\}_2(Aspc)]$	Green	36.15 (36.21)	5.80 (5.77)	8.50 (8.44)	19.40 (19.33)	200
	HApBH	White	70.26 (70.28)	5.50 (5.48)	17.54 (17.56)	—	165
4	$[Ni\{(MeO)_2PS_2\}(ApBH)]$	Brown	42.25 (42.32)	4.05 (4.00)	9.20 (9.25)	14.20 (14.12)	180
5	$[Ni\{(EtO)_2PS_2\}(ApBH)]$	Brown	44.90 (44.84)	4.54 (4.60)	8.77 (8.71)	13.40 (13.30)	190
6	$[Ni\{(PrO)_2PS_2\}(ApBH)]$	Greenish yellow	47.15 (47.08)	5.20 (5.14)	8.18 (8.24)	12.50 12.57	190

TABLE II IR Spectra of the Complexes and HApBH

No.	ν_{NH_2}	ν(NH)	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{C=N_p}$	ν_{N-N}	ν_{C-O}	Dithiophosphate moiety			M–O	M–N	M–S
								$\nu_{p\text{.....}S_{(asy)}}$	$\nu_{p\text{.....}S_{(s)}}$	ν_{P-O}			
1	3450, 3370	3250	1680	1585	1560	1015	—	690	600	1010, 940	550	420	510
2	3460, 3380	3280	1675	1590	1565	1015	—	685	590	1010, 930	555	415	495
3	3445, 3390	3285	1665	1590	1575	1025	—	680	590	1020, 960	550	430	490
HApBH	—	3200	1645	1600	1540	980	—	—	—	—	—	—	—
4	—	—	1610	1580	1550	1015	1430	680	600	1010, 960	535	425	505
5	—	—	1620	1585	1575	1020	1435	685	590	1010, 960	540	425	490
6	—	—	1620	1585	1573	1015	1440	685	595	1010, 940	540	420	485

1. The IR spectra of 2-acetylpyridine semicarbazone complexes (**1–3**) show two bands in the ranges 3370–3390 cm^{-1} and 3445–3460 cm^{-1} which are assigned to the symmetric and asymmetric stretching modes of NH_2, indicating the noninvolvement of this group in coordination. A strong band appears in the region 1585-1590 cm^{-1}; suggesting that Apsc ligand coordinates through the nitrogen atom of azomethine group.[5] Bands of strong intensities around 1665–1680 cm^{-1} in the spectra of the above complexes may be attributed to $\nu(C=0)$. The frequency lowering of this band from 1760 cm^{-1} [18] in the ligand to 1665–1680 cm^{-1} in the spectra of the complexes demonstrates the participation of the carbonyl group in coordination.[5] Moreover, bands observed in the region 3250–3285 cm^{-1} are attributed to νNH of the imino group, confirming its nonparticipation in coordination. Thus, the 2-acetylpyridine semicarbazone is found to act as neutral bidentate ligand in complexes (**1**), (**2**), and (**3**); coordinating through oxygen of the carbonyl group (ketoform) and nitrogen atom in the azomethine group.[5]
2. In the IR spectrum of 2-acetylpyridine-benzoylhydrazone ligand (HApBH), the band at 3200 cm^{-1} may be assigned to νNH of the imino group and the sharp bands located at 1600, 1645, and 980 cm^{-1}, may be attributed respectively to the $\nu_{C=N}$, $\nu_{C=O}$ and ν_{N-N} modes.[19,20] Moreover, there are some bands appear at 1540, 1040, 660, and 440 cm^{-1} are attributed to $\nu_{C=C+C=Np}$ of the pyridyl ring.[21]

   Two tautomeric forms, the keto form structure (III) and the enol form structure (IV), can represent HApBH.



(III) (IV)

3. The comparative study of the infrared spectra of the mixed complexes and the free ligand can be performed only on the main bands (Table II). The IR spectra for the complexes (**4–6**) exhibit a band at 1580–1585 cm^{-1} due to $\nu_{C=N}$. This is shifted to lower frequency, suggesting that this group takes part in coordination. The coordination of nitrogen to the metal atom would be expected to reduce the electron density on the azomethine link and thus cause a shift in the $\nu_{C=N}$ band. The small shift to higher frequency of the band at (1015–1020 cm^{-1}) and (980 cm^{-1} in the ligand) due to ν_{N-N}[22] can be taken as additional evidence for the participation of the azomethine

group in bonding. All these changes in amide group vibrations reveal the involvement of the amide oxygen in coordination by loss of one proton. This result is confirmed by the presence of a new band at 535–540 cm^{-1}, ascribed to ν_{M-O}.[23,24] However, the intensity of νNH band decreased in the complexes (**4–6**); the new band appears at 1430–1440 cm^{-1} and may be due to ν_{C-O}.

From IR spectra for the complexes (**4–6**) we can conclude that HApBH behaves as mononegative tridentate ligand, coordinating through carbonyl oxygen in the enol form, azomethine nitrogen, and acetylpyridine ring nitrogen,[25] which was confirmed from the shift of $\nu_{C=Np}$ to higher frequency.

4. There are some bands in the IR spectra of all the complexes (**1–6**) characteristic of dithiophosphate group: (a) Two bands appear in the two regions 590–600 and 680–690 cm^{-1}; these bands are assignable to the symmetric and asymmetric stretching frequencies of P–S band,[15,26] (b) The P–O stretching frequency occurs at 930–1020 cm^{-1}, this band was observed as one or two bands.[15]

Support of the above interpretation is the appearance of the absorption frequencies $\nu_{(M-O)}$,[23,24] $\nu_{(M-N)}$,[27] and $\nu_{(M-S)}$[26] at 535–555, 415–430, and 485–510 cm^{-1} respectively.

ELECTRONIC SPECTRA

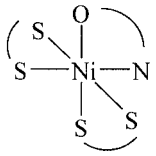
The electronic spectra for all the complexes are recorded in DMF and listed in Table III. The electronic spectra of all complexes (**1–6**) are similar, where they consist of three types of transition. (1) Two d-d transition

TABLE III Electronic Spectral Bands of the Complexes and their Assignments (cm^{-1})

No.	d–d Transition	Charge transfer Transition	Intraligand Transition
1	11,455, 16,148	26,182, 32,734	37,595
2	11,712, 15,173	25,640, 32,250	38,763
3	12,360, 15,310	25,710, 32,780	37,590
4	11,830, 14,920	25,600, 32,460	37,730
5	11,730, 16,550	25,700, 33,220	37,730
6	11,330 16,180	25,570, 32,780	37,920

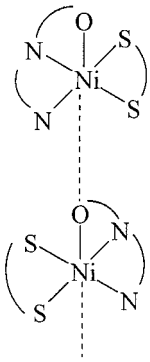
bands appear in two regions 11,330–12,360 and 14,920–16,550 cm^{-1} assignable to $^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (ν_2) transition respectively. These transitions correspond to an octahedral structure around Ni(II) in the complexes. The six-coordination geometry may be attained through molecular association in the complexes. (2) The second type of transitions occurs with high intensity in the range 25,570–33,220 cm^{-1} and is assigned to charge-transfer[28] transitions. (3) The intraligand transitions are located in the range 37,595–38,763 cm^{-1}; they may correspond to n-π^* transitions.[29]

From the forgoing data, the following structures can be postulated for the complexes



Proposed structure of the complexes
[Ni {$(RO)_2 PS_2$}$_2$ (Apsc)]

= 2-acetylpyridine semicarbazone



Molecular association of the complexes
[Ni{$(RO)_2 PS_2$}(ApBH)]

= dialkyldithiophosphate anion

= 2-acetylpyridine benzoylhydrazone anion

THERMAL ANALYSIS

The thermogravimetric analysis behavior of the complexes **1–6** is divided according to the second ligand:

(a) The first type represented by complex **2** (Figure 1). The TG and DTG thermograms for this complex consist of two stages. The first weight loss occurs at 105°C, correlated to 18.2% and is attributed to elimination of four ethylene molecules (calc. 18.5%)

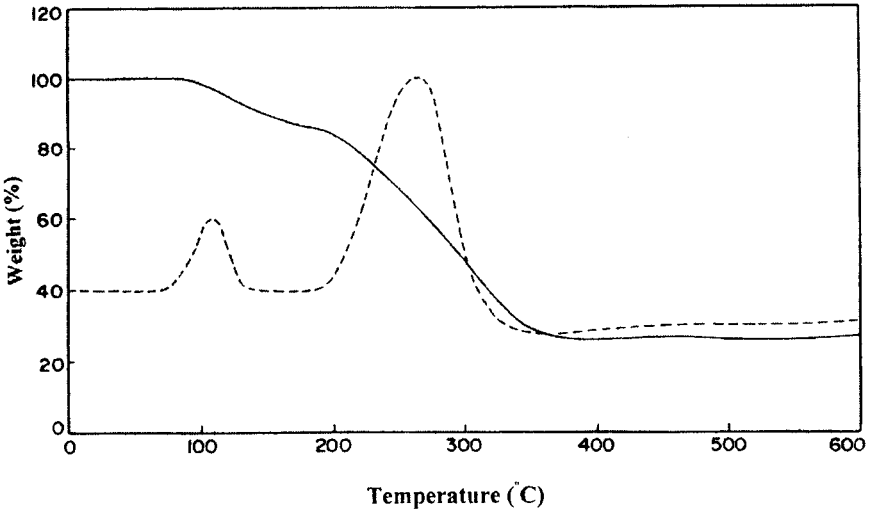


FIGURE 1 TG (—) and DTG (----) thermograms of [Ni $\{(EtO)_2PS_2\}_2$ (Apsc)].

from diethyldithiophosphate moiety forming the unstable compound [Ni$\{(OH)_2PS_2\}_2$(Apsc)]. The last complex decomposes at 270°C forming Ni_2O_3 as the final product. Elimination of alkenes from dialkyldithiophosphate is known previously.[30] The mechanism of this thermal decomposition could be proposed as follows:

$$[Ni\{(RO)_2PS_2\}_2Apsc] \xrightarrow{-alkene} [Ni\{(OH)_2PS_2\}_2Apsc] \qquad (3)$$

where

R = ethyl or n-propyl.

(b) An examination of the TG and DTG curves (Figure 2) of the ligand 2-acetylpyridine benzoylhydrazone (HApBH) indicates that the curve consists of three decomposition steps at 260, 325, and 465°C. The first step seems to be associated with the expulsion of the radical $C_7H_8N_3$ (calc. 56.0%, found 56.1%), which may take $H^\bullet$ forming $C_7H_9N_3$ molecule. The second step is small and the mass loss correlates well with the evolution of carbon monoxide molecule (calc. 11.7%, found 11.8%) leaving a phenyl radical C_6H_6 which decomposes in final stage.

It is of interest to note that the thermal decomposition of the ligand (HApBH) beers some resemblance to the fragmentation pattern

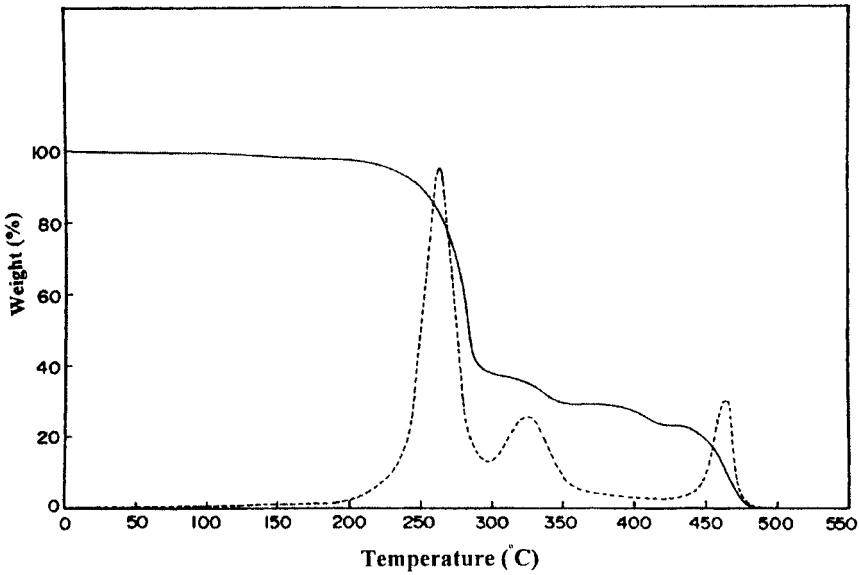
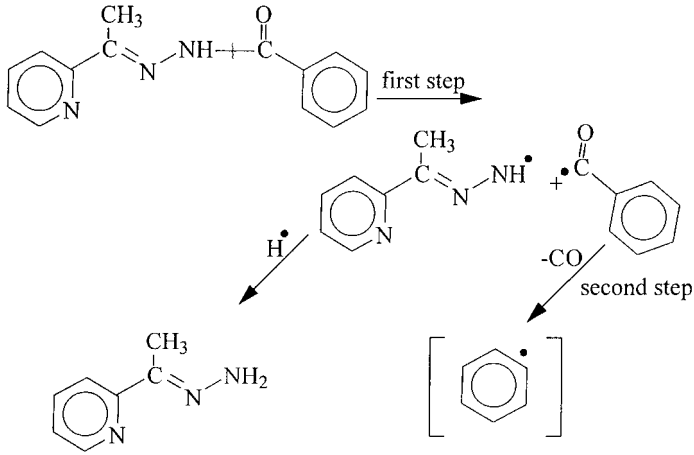


FIGURE 2 TG (—) and DTG (----) thermograms of HApBH.

of its mass spectrum and the mechanism of this thermal decomposition may be represented as:



(c) The second type of the complexes according to the behavior of thermal analysis can be represented by complex **6** (Figure 3). The TG and DTG thermograms of compound **6** contain three decomposition steps. The first (150°C) and second (240°C) steps recorded are

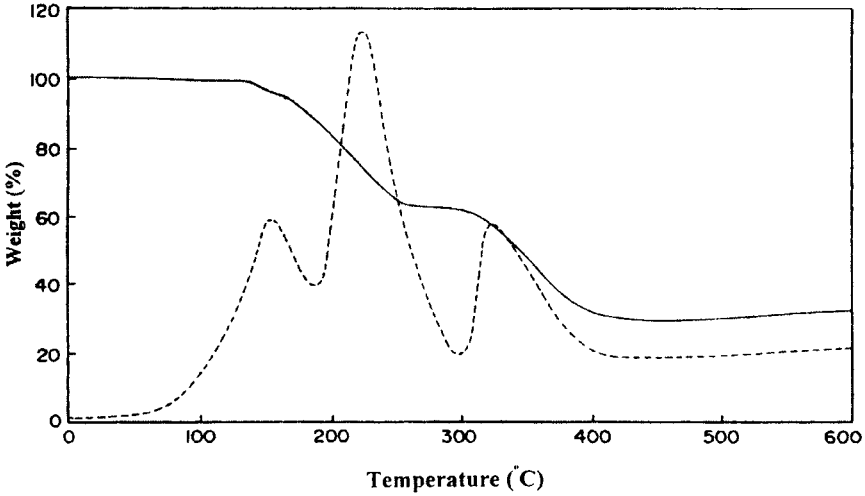


FIGURE 3 TG (—) and DTG (----) thermograms of [Ni $\{(EtO)_2PS_2\}$ (ApBH)].

related to elimination of 2 $CH_2{=}CH_2$ molecules and $C_7H_7N_2$ radical (calc. 36.5% found 37%) to form an unstable complex which decomposes at 330°C with nickel oxide as the end product. The rupture of N—N bond during thermal decomposition of hydrazones is known in literature.[31]

The mechanism of the thermal decomposition for complex **6** could be suggested as following

MASS SPECTROMETRY

The mass spectral fragmentation pattern of [Ni$\{(EtO)_2PS_2\}_2$(Apsc)] is depicted in Scheme 1. One branch (a) of this scheme represents a series

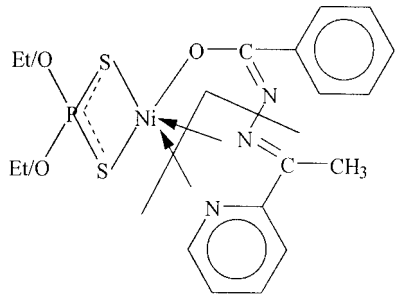
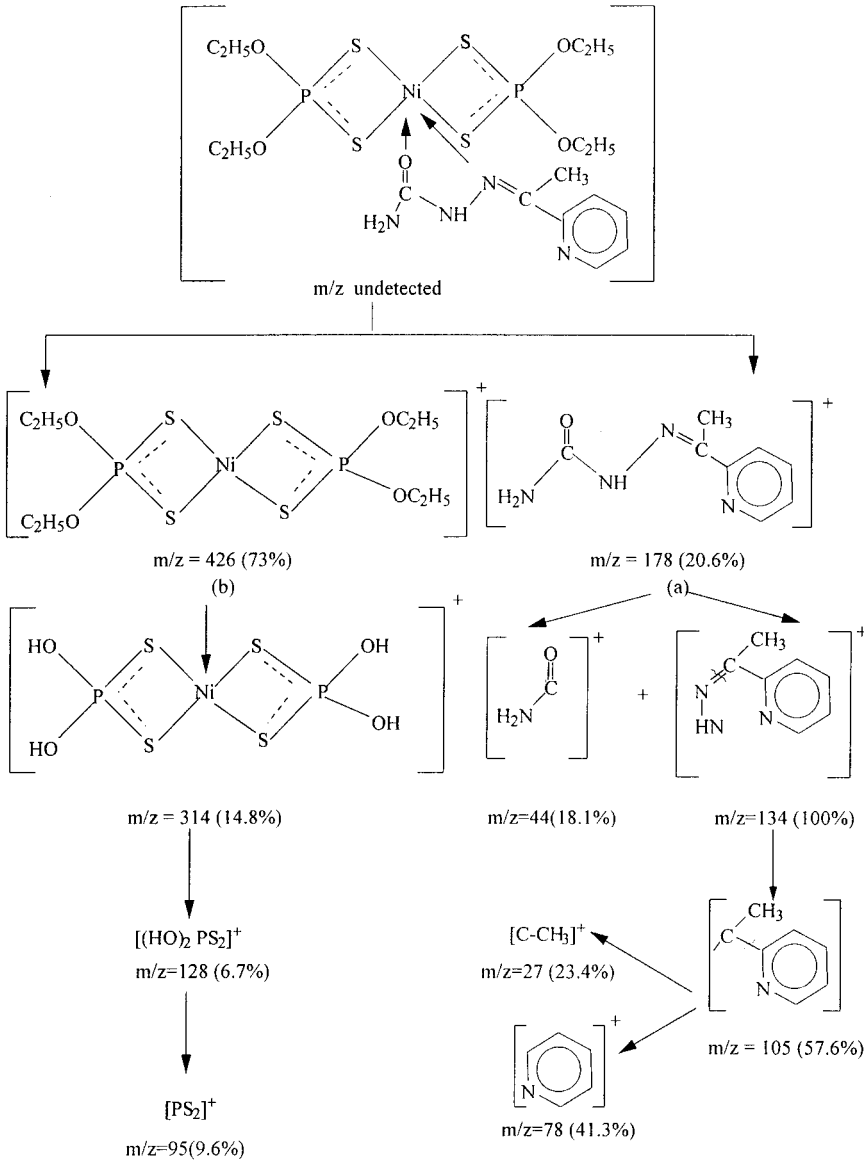


FIGURE 4 Proposed thermal decomposition of the complex [Ni-$\{(EtO)_2\}PS_2$(ApBH)].

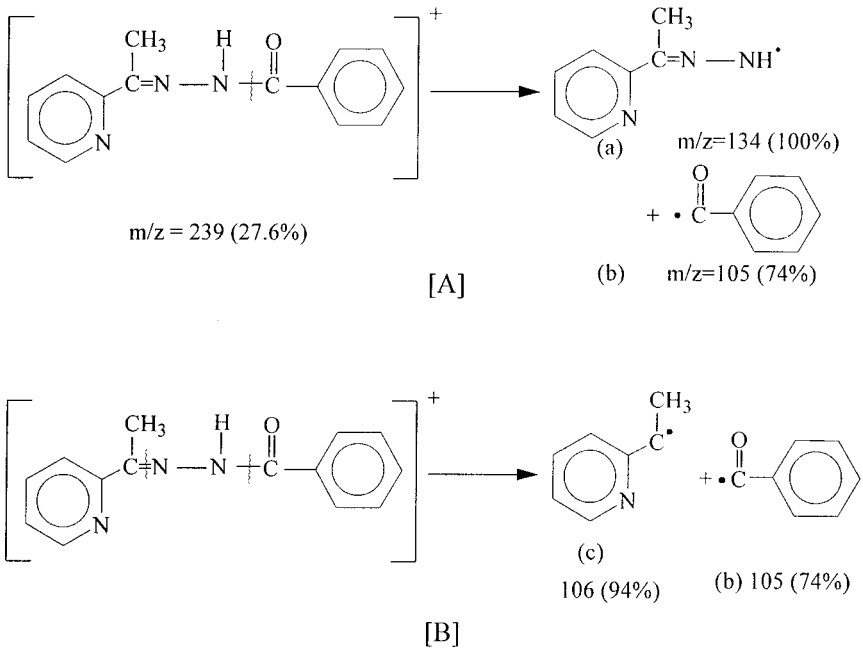


SCHEME 1

of fragments, corresponding to fragmentation of 2-acetylpyridine semicarbazone that loses a $[NH_2{-}CO]^+$ forming the species $[C_7H_8N_3]^+$ m/z = 134. This ion represents the base peak indicating its higher stability; finally the fragment ions $[C{-}CH_3]^+$ with m/z = 27 (23.4%)

and pyridine $[C_5H_4N]^+$ m/z = 78 (41.3%) are formed. The other branch (b) includes a nickel(II)bis(diethyldithiophosphate) fragment ion $[NiC_8H_{20}O_4P_2S_4]^+$ of m/z = 426 (73%) which losses four ethylene molecules leading to the formation of $[Ni\{(OH)_2PS_2\}_2]^{+(30)}$ with m/z = 314 (14.8%) and the final fragment ion $[PS_2]^+$ of m/z = 95 (9.6%) is formed.

The mass spectrum of the ligand (HApBH) exhibits the molecular ion $[M^+]$ with intensity (27.6%) and m/z = 239. The mass spectral fragmentation of the ligand is recorded in Scheme 2. We suggest two fragmentation pathways, which are followed by this molecular ion. First one [A] includes a strong intensity peak at m/z = 134(100%). This can be ascribed to the fragment ion (a) resulting from the elimination of benzoyl fragment (b) which is characterized by m/z = 105 and (74%). The second pathway [B] includes the cleavage occurring on —N—C— and —C=N[25] by elimination of the diazo group. This can be attributed to formation of the fragment ion (b) m/z = 105 (74%) and (c) m/z = 106 (94%) as shown in Scheme 2. Some fragments were detected for similar compounds in the literature.[25]



SCHEME 2

TABLE IV Antibacterial and Antifungal Activity of Apsc, HApBH, and Some Complexes (The diameter of the inhibition zone in mm.)

Compound	Antibacterial activity			Antifungal activity			
	B. cereus (Give)	*M. lutes* (G+ve)	*Streptonyces* (G+ve)	*A. spergilus flovus*	*Fusarium oxysporium*	*Chrysosporium Tropicm*	*A. funig. var. albus*
Apsc	10	12	15	10	10	18	0
$[Ni\{(PrO)_2PS_2\}_2Apsc]$	12	10	12	12	10	12	15
HApBH	16	15	30	22	20	25	22
$[Ni\{(PrO)_2PS_2\}(ApBH)]$	12	0	9	10	15	12	15
Erythromycin	0	0	0	0	0	0	0

MICROBIOLOGICAL SCREENING

The biological activities of the two organic ligands (Apsc and HApBH), some related complexes and Erythromycine (as a reference compound) were tested against a number of bacteria and fungi. The used bacteria were *B. cereus* G+ve, M. *luteus* G+ve, and *Streptonyces* G+ve; the tested fungi were *Asperrgillus flovus, Fusarium oxysporium, Chrysosporium tropicm*, and *A. fumig. var. albus.* The culture media used were nutritent agar (N.A.) media supplemented with one GM yeast/liter. The antimicrobial activity of each compound was evaluated by the classical filter paper disc technique. Each of the compounds was dissolved in dimethylformamide (DMF) and a solution with the concentration 0.5-mg $ml^{-1}$was prepared. The organic compound (HApBH) shows a high degree of activity against bacteria and fungi (Table IV). This activity may be due to the pyridyl ring and OH group in the compound (Enol form); which play an important role in the antibacterial[25] and antifungal activity.

CONCLUSION

The spectroscopic data show that the 2-acetylpyridine semicarbazone (Apsc) acts in the complexes $[Ni\{(RO)_2PS_2\}_2(Apsc)]$ (R=methyl, ethyl, or n-propyl) as a bidentate ligand through C=N nitrogen and oxygen of C=O group. However, 2-acetylpyridine benzoylhydrazone (HApBH) coordinates as a mononegative tridentate ligand in the complexes $[Ni\{(RO)_2PS_2\}(ApBH)]$ where the coordination occurs through enolic oxygen, azomethine nitrogen, and acetylpyridine ring nitrogen. An octahedral structure for all the complexes was postulated.

The thermoanalytical results of the first type of the complexes prove that the main feature of the first decomposition step is the evolution of alkene molecules and the final product is Ni_2O_3. However the TG and DTG thermograms of the HApBH ligand consist of three decomposition steps. The first and second steps are associated with the expulsion of $C_7H_8N_3$ radical and carbon monoxide respectively. Moreover, the behavior of thermal analysis of the second type of the complexes shows that the weight loss of the first step is related to elimination of alkenes and $C_7H_7N_2$radical and the final product is Ni_2O_3.

The mass spectral fragmentation pattern of $[Ni\{(EtO)_2PS_2\}_2(Apsc)]$ exhibit fragmentation of Apsc and $[Ni\{(EtO)_2PS_2]^+$ fragment ion. However, the mass spectrum of the HApBH gave the molecular ion of the ligand $[M^+]$, which decomposed to two main fragments. The HApBH ligand has a high toxicity against the bacteria and fungi under study;

this may be due to presence of pyridyl ring and hydroxyl group in the compound.

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