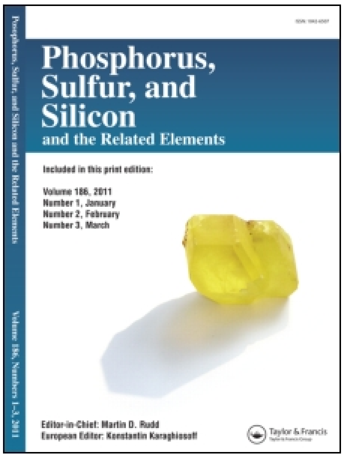


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STUDIES OF MIXED LIGAND COMPLEXES FROM DIALKYLDITHIOPHOSPHATE AND THIOSEMICARBAZIDE OR THIOSEMICARBAZONES WITH NICKEL(II)

Amna S. A. Zidan[a]; Asma I. El-Said[a]
[a] Assiut University, Assiut, Egypt

To cite this Article Zidan, Amna S. A. and El-Said, Asma I.(2004) 'STUDIES OF MIXED LIGAND COMPLEXES FROM DIALKYLDITHIOPHOSPHATE AND THIOSEMICARBAZIDE OR THIOSEMICARBAZONES WITH NICKEL(II)', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 7, 1293 — 1305

To link to this Article: DOI: 10.1080/10426500490468100

URL: http://dx.doi.org/10.1080/10426500490468100

Phosphorus, Sulfur, and Silicon, 179:1293–1305, 2004
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490468100

STUDIES OF MIXED LIGAND COMPLEXES FROM DIALKYLDITHIOPHOSPHATE AND THIOSEMICARBAZIDE OR THIOSEMICARBAZONES WITH NICKEL(II)

Amna S. A. Zidan and Asma I. El-Said
Assiut University, Assiut, Egypt

(Received September 4, 2003; accepted November 7, 2003)

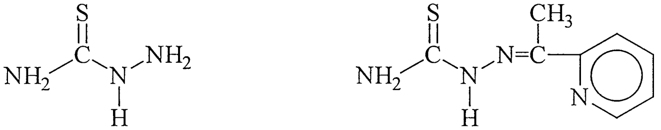
The complexes [Ni{$(RO)_2PS_2$}$_2$Tsc], [Ni{$(RO)_2PS_2$}$_2$ApTsc], and [Ni{$(RO)_2PS_2$}FurTsc.$2H_2O$] where R = methyl (Me), ethyl (Et) or propyl (Prop); Tsc = thiosemicarbazide, ApTsc = 2-acetylpyridinethiosemicarbazone, and FurTsc = furfuraldhydethiosemicarbazone have been synthesized and characterized by elemental analysis, conductance measurements, and spectral studies (IR, UV-Vis, and mass). Thermal studies of the complexes have been carried out using TG and DTG techniques. An octahedral structure has been proposed for all types of the complexes. A representative types of the complexes are tested against various pathogenic bacteria and fungi. The [Ni{$(EtO)_2PS_2$}$_2$ApTsc] shows a high degree of activity against bacteria and fungi; this may be attributed to the pyridyl ring of the 2-acetylpyridinethiosemicarbazone ligand.

Keywords: Dithiophosphate; nickel(II) complexes; thermal behavior; thiosemicarbazide; thiosemicarbazones

Thiosemicarbazide and thiosemicarbazones have attracted special attention due to their biological activities.[1–4] These compounds present a wide variety of biological activity such as antitumoral,[5–8] fungicidal,[9,10] bactericidal,[11] and antiviral.[7] It is known that some drugs have increased activity when administered in the form of the metal complexes,[12,13] and a number of metal chelates inhibit tumor growth.[14] In the treatment of cancer, the active species is not the thiosemicarbazone but its metal chelates.[14] Chemically, heterocyclic thiosemicarbazones are of interest because of their great versatility as ligands, which derives from the presence of several potential donor atoms, their

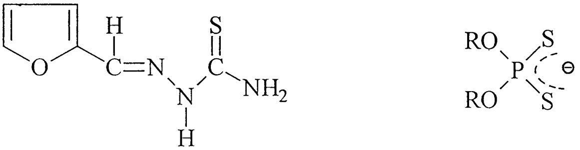
---

Address correspondence to Amna S. A. Zidan, Chemistry Department, Faculty of Sciences, Assiut University, Assiut 71516, Egypt. E-mail: amna@aun.edu.eg



Thiosemicarbazide (Tsc)

2-Acetylpyridinethiosemicarbazone (ApTsc)



Furfuraldehydethiosemicarbazone (FurTsc)

R= methyl (Me)
= ethyl (Et) or
= propyl (Prop) dithiophosphato anion

FIGURE 1 Structures of the ligands.

flexibility, and their ability to coordinate in either neutral or deprotonated forms.[15]

The chemistry study of the metal complexes that contain bidentate sulphur donor ligand was very interesting because it plays an important role in analytical and structural aspects of coordination chemistry.[16–19] In continuance of our work on the coordination chemistry of dialkyldithiophosphates,[20,21] we describe here the synthesis and structural characterization of new types of mixed ligand complexes between bis(dialkyldithiophosphato)nickel(II) and thiosemicarbazide (Tsc), 2-acetylpyridinethiosemicarbazone (ApTsc), or furfuraldehydethiosemi-carbazone (FurTsc) (Figure 1).

EXPERIMENTAL

All the reagents viz., thiosemicarbazide, furfuraldehyde (Fluka) and 2-acetylpyrdine (Merck) are of analytical grade and were used as received. Bis(dialkyldithiophosphato)nickel(II)[22] and the Schiff bases were prepared by the condensation of aldehyde or ketone with thiosemicarbazide in 1:1 molar ratio in absolute ethanol.[23]

Physical Measurements

The electronic spectra (in DMF) were recorded on an UV-2101 PC Shimadzu spectrophotometer. The infrared spectra were recorded on a 470 Shimadzu infra-red spectrophotometer as KBr discs. The elemental analyses data were obtained by Analytischer Funktions-test Vario El-Fab-Nr. 11982027 apparatus. JEOL-JMS$_{600}$ apparatus was used for recording the mass spectra. Thermal measurements were carried out on a 2000 Dupont thermal analyzer, the heating rate was 10 deg/min.

Synthesis of the Complexes

A hot ethanolic solution of either thiosemicarbazide (0.91 g, 0.01 mmol), 2-acetylpyrdinethiosemicarbazone (1.94 g, 0.01 mmol), or furfuraldehydethiosemicarbazone (1.78 g, 0.01 mmol) was added to a chloroform solution of 3.81 g (0.01 mmol), 4.26 g (0.01 mmol) or 4.83 (0.01 mmol) of bis(dimethyldithiophosphato), bis(diethyldithiophosphato)-, or dipropyldithiophosphato)nickel(II) respectively. The mixture was stirred for 2 h, where upon the color was changed from violet to green or yellow. The resulting solids were separated after two days, and then filtered, washed several times with diethyl ether, and air dried.

RESULTS AND DISCUSSION

The mixed ligand complexes may be formed according to the following equations:

$$[\mathrm{Ni}\{(\mathrm{RO})_2\mathrm{PS}_2\}_2] + \mathrm{Tsc} \rightarrow [\mathrm{Ni}\{(\mathrm{RO})_2\mathrm{PS}_2\}_2\mathrm{Tsc}] \quad (1)$$

$$[\mathrm{Ni}\{(\mathrm{RO})_2\mathrm{PS}_2\}_2] + \mathrm{ApTsc} \rightarrow [\mathrm{Ni}\{(\mathrm{RO})_2\mathrm{PS}_2\}_2\mathrm{ApTsc}] \quad (2)$$

$$[\mathrm{Ni}\{(\mathrm{RO})_2\mathrm{PS}_2\}_2] + \mathrm{HFurTsc} \rightarrow [\mathrm{Ni}\{(\mathrm{RO})_2\mathrm{PS}_2\}\mathrm{FurTsc}] + (\mathrm{RO})_2\mathrm{PS}_2\mathrm{H} \quad (3)$$

where R = CH_3-, C_2H_5- or C_3H_7- and Tsc = thiosemicarbazide; ApTsc = 2-acetylpyridinethiosemicarbazone, HFurTsc = furfuraldehydethiosemicarbazone.

All the prepared complexes are stable in air and partially soluble in common organic solvents. Analyses of the complexes were presented in Table I. The analytical data are in a good agreement with the proposed stoichiometry of the complexes. The Tsc and ApTsc ligands coordinate with Ni(II) as a bidentate through the amino or azomethine nitrogen and sulphur atoms in a neutral form, respectively, HFurTsc, however coordinates as a mononegative ligand through the same donor atoms. The poor molar conductivity values of all complexes (7–9 $\Omega^{-1} \cdot \mathrm{cm}^2 \cdot \mathrm{mol}^{-1}$) indicate that these complexes are nonelectrolytes.

TABLE I Physical, Characteristics and Analytical Data of the Complexes

No.	Compound	Color	Elemental analysis found (Calc. %) C	H	N	S	Dec. p °C
1	[Ni{(MeO)$_2$PS$_2$}$_2$Tsc]	Blue	12.95 (12.93)	3.70 (3.69)	9.08 (9.05)	34.55 (34.53)	320
2	[Ni{(EtO)$_2$PS$_2$}$_2$Tsc]	Blue	20.80 (20.78)	4.85 (4.84)	8.10 (8.08)	30.80 (30.81)	330
3	[Ni{(PropO)$_2$PS$_2$}$_2$Tsc]	Blue	27.10 (27.09)	5.76 (5.77)	7.30 (7.29)	27.78 (27.80)	335
4	[Ni{(MeO)$_2$PS$_2$}$_2$ApTsc]	Brown	25.38 (25.40)	3.90 (3.91)	9.90 (9.88)	28.28 (28.26)	350
5	[Ni{(EtO)$_2$PS$_2$}$_2$ApTsc]	Brown	30.85 (30.83)	4.86 (4.85)	9.00 (8.99)	25.72 (25.71)	365
6	[Ni{(PropO)$_2$PS$_2$}$_2$ApTsc]	Yellow	35.32 (35.35)	5.63 (5.64)	8.23 (8.25)	23.61 (23.59)	373
7	[Ni{(MeO)$_2$PS$_2$}FurTsc · 2H$_2$O]	Green	22.46 (22.49)	3.77 (3.78)	9.82 (9.84)	22.50 (22.52)	310
8	[Ni{(EtO)$_2$PS$_2$}FurTsc · 2H$_2$O]	Green	26.43 (26.41)	4.45 (4.43)	9.26 (9.24)	21.17 (21.15)	315
9	[Ni{(PropO)$_2$PS$_2$} FurTsc ·2H$_2$O]	Yellowish	29.83 (29.82)	5.02 (5.01)	8.62 (8.60)	19.93 (19.90)	315

Tsc = Thiosemicarbazide. ApTsc = 2-Acetylpyridinethiosemicarbazone. FurTsc = Furfuraldehydethiosemicarbazone anion.

IR Spectra

The characteristic frequencies of the two coordinated ligands in the mixed ligand complexes are listed in Table II and can be assigned as follows:

a) Two bands appearing in the regions 3290–3300 and 3090–3095 cm^{-1} in the spectra of the complexes of the type [Ni{(RO)$_2$PS$_2$}$_2$Tsc] were attributed to the asymmetric and symmetric modes of the NH$_2$ group respectively. This band is reported at 3400 and 3100 cm^{-1} in the Tsc ligand.[24] This shift in frequency indicates the involvement of this group in coordination. A strong band at 810 cm^{-1} in the ligand (Tsc) is mainly due to υ(C=S) stretching frequency;[25] this band is observed in the complexes around 780–800 cm^{-1}. It is expected that the strong band which appears in 1180–1190 cm^{-1} for the mixed ligand complexes region has some contribution from the C=S stretching frequency;[26] υ(N—C—N) stretching vibration,[27] or υ(N—N) stretching and δ(N—C—N) deformation vibrations.[28–30] These bands are shifted generally toward the lower frequency side in the spectra of

TABLE II IR Spectral Data of the Complexes (cm^{-1})

	Alkyldithiophosphate moiety			Thiosemicarbazone moiety					
No.	$\upsilon(\mathrm{P{-}S})_{(\mathrm{asy})}$	$\upsilon(\mathrm{P{-}S})_{(\mathrm{sy})}$	$\upsilon(\mathrm{P{-}O})$	$\upsilon(\mathrm{NH_2})$, $\upsilon(\mathrm{NH})$, $\upsilon(\mathrm{H_2O})$	$\upsilon(\mathrm{C{=}N})$	$\upsilon(\mathrm{C{=}S})$	$\upsilon(\mathrm{C{-}S})$	M—N	M—S
1	640	530	1000	3300, 3095	—	1190, 800	—	430	500
2	660	540	1010	3290, 3090	—	1180, 780	—	420	495
3	660	530	1020	3300, 3090	—	1190, 800	—	435	505
4	665	540	970	3380, 3180	1610	1180, 810	—	430	490
5	670	550	1010	3380, 3175	1610	1170, 830	—	425	510
6	650	540	1015	3380, 3180	1605	1180, 810	—	440	500
7	670	530	990	3375, 3175, 3400	1615	—	1020	435	490
8	670	550	985	3370, 3170, 3420	1610	—	1015	440	485
9	680	560	990	3380, 3175, 3410	1615	—	1015	440	495

the complexes, (related to Tsc) indicating that the coordination is taking place through the ketonic sulphur atom.

b) The IR spectrum of the 2-acetylpyridinethiosemicarbazone (ApTsc) ligand exhibits some bands at 3380, 3180, 1200 and 830 cm^{-1} which are attributed to $\upsilon(NH_2)$, $\upsilon(NH)$ and $\upsilon(C{=}S)$, respectively,[24,25] in the thion form (Figure 1). The same bands were observed in the regions, 3380, 3175–3180, 1170–1180 and 810–820 cm^{-1} in the complexes of the type $[Ni\{(RO)_2PS_2\}_2ApTsc]$. This clearly indicates the non-involvement of the NH_2 group in coordination.[30] However, the azomethine and C=S groups participate in this coordination.[26] Moreover, a strong band at 1650 cm^{-1} in the spectrum of the ligand is assigned to $\upsilon(C{=}N)$. This band shifts to a lower frequency by 40–45 cm^{-1}. This shift to lower frequency indicates the involvement of the azomethine nitrogen in bonding to the metal ion. Thus, the ligand acts as a neutral bidentate NS donor.[26]

c) The complexes of the type $[Ni\{(RO)_2PS_2\}FurTsc{\cdot}2H_2O]$ exhibit $\upsilon(OH)$ and $\rho(H_2O)$ bands in the 3400–3420 and 680–690 cm^{-1} regions which are indicative of coordinated water in the complexes.[31,32]

Neither the ligand HFrTsc nor its complexes show absorption bands between 2000 and 2500 cm^{-1}, suggesting that no S—H bonding. The spectrum of the ligand exhibits bands at 3360, 3200 and 830 cm^{-1} which were attributed to $\upsilon(NH_2)$, $\upsilon(NH)$ and $\upsilon C{=}S)$,[24,25] respectively. In the complexes, $\upsilon(NH)$ and $\upsilon(C{=}S)$ disappear and accompanied by the appearance of $\upsilon(C{-}S)$ at 1015–1020 cm$^{-1.33,34}$ Thus, indicates that the ligand undergoes there in enol form which deprotonated on complexation and coordinates through the thiolate sulphur as anion. Further, in the ligand spectrum, the strong band observed at 1600 cm^{-1} can be assigned to $\upsilon(C{=}N)$ frequencies. This shifts to higher frequency region 1610–1615 cm^{-1} in the spectra of the complexes, indicating coordination of nitrogen of the azomethine group to the metal ion.[35,36]

Moreover, all complexes show strong two bands in the two regions 985–1020 and 640–680 cm^{-1}, which are assigned to $\upsilon(P{-}O)$ and $\upsilon(P{-}S)$, respectively,[20,21,37] in the dithiophosphate group.

The important features of the infrared spectra of all the complexes are the appearance of two strong bands at 420–440 cm^{-1} and 485–510 cm^{-1}, which may be assigned to $\upsilon(M{-}N)$ and $\upsilon(M{-}S)$ bands respectively.[37,39]

Electronic Spectra

The electronic spectra of the complexes display two bands at 14,663–16,779 and 19,342–21,413 cm^{-1} regions (Table III). These spectral

TABLE III Electronic Spectral Bands for the Complexes in (cm^{-1})

No.	d-d Transition	Intraligand and charge transfer bands
1	16,779; 21,008	33,333; 41,667; 48,077
2	16,556; 21,413	33,671; 38,462; 48,309
3	16,393; 20,964	33,670; 41,841; 46,729
4	14,837; 19,417	31,153; 49,261
5	14,663; 19,417	31,348; 43,103; 49,020
6	14,749; 19,342	31,250; 43,290; 46,729
7	15,015; 20,576	31,153; 43,478; 48,780
8	15,038; 20,661	32,895; 49,020
9	15,054; 20,618	31,153; 46,729

bands may be assigned to $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (υ_2) and $^3A_{2g} \rightarrow {}^3T_{1g}$(P) ($\upsilon_3$) transitions, respectively, and supports the octahedral structure for the complexes. The second type of bands which appear in the range 31,153–33,671 cm^{-1} are assigned to π-π^* transition of azomethine chromophores[38]. Bands appearing in the region 41,667–49,261 cm^{-1} are assigned to π-π^* transition[39] of the different moieties of thiosemicarbazone ligands.[39]

From the forgoining data we suggest the structures for the complexes (Figure 2).

Mass Spectra

The mass spectrum of [Ni{EtO)$_2$PS$_2$}$_2$ApTsc] complex shows the molecular ion peak at m/z = 620 [M]$^+$. The mass spectral fragmentation of

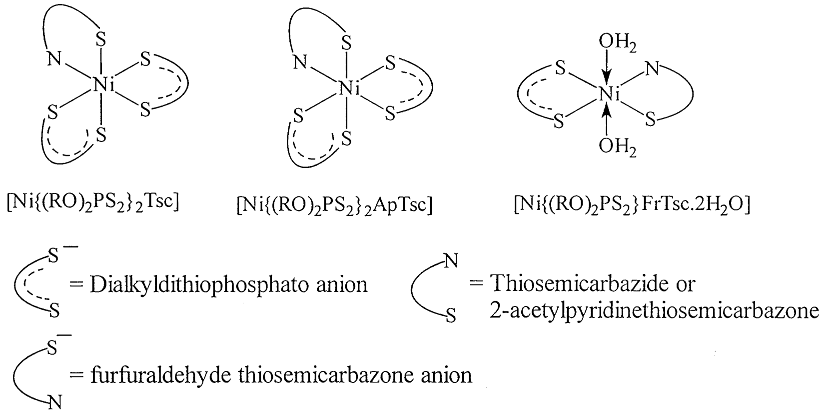
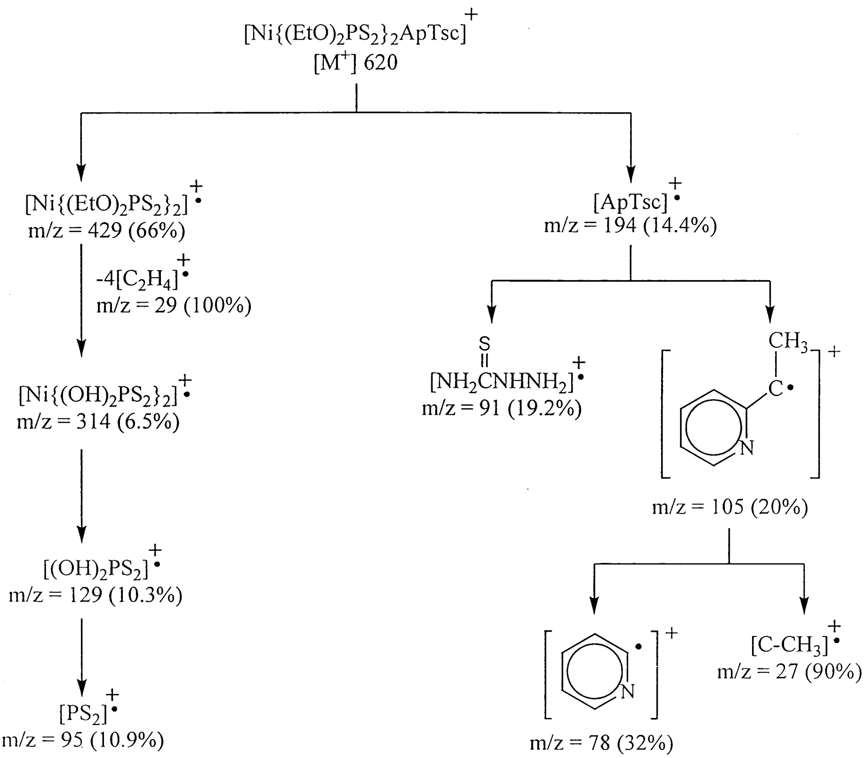


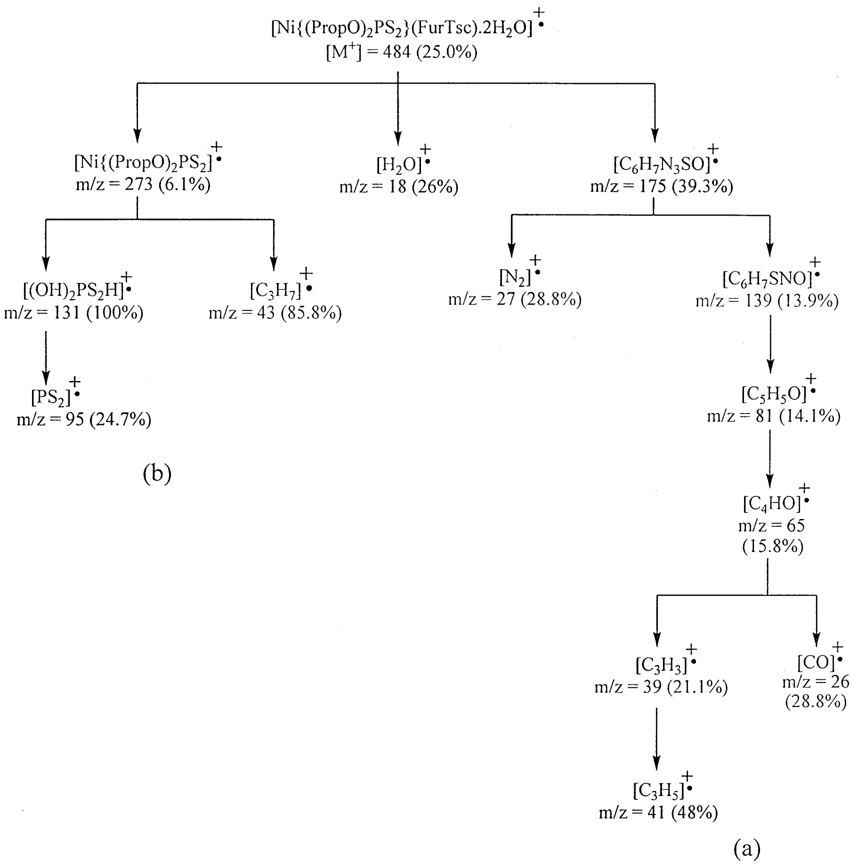
FIGURE 2 Suggested structures of the complexes.



SCHEME 1

this complex is recorded in Scheme 1. The molecular cation during fragmentation process loses the 2-acetylpyridinethiosemicarbazone ligand under FAB conditions to give species such as 429 $[Ni\{(EtO_2)_2PS_2\}_2]^{+\cdot}$; 314 $[Ni\{(OH)_2PS_2\}_2]^{+\cdot}$; 129 $[(OH)_2PS_2]^{+\cdot}$ and 95 $[PS_2]^{+\cdot}$[21] after elimination of $[CH_2{=}CH_2]^{+\cdot}$ and nickel atom. Moreover, the fragments of 2-acetypyridinethiosemicarbazone are 91 $[CH_3N_3S]^{+\cdot}$; 105 $[C_7H_7N]^{+\cdot}$; 78 $[C_5H_5N]^{+\cdot}$ and 27 $[C_2H_3]^{+\cdot}$ which observed in the literature.[21]

The mass spectral fragmentation pattern of $[Ni\{(PropO)_2PS_2\}\text{-}FurTsc\cdot 2H_2O]^{+\cdot}$ is depicted in Scheme 2. One branch (a) of this scheme represents a series of fragments, corresponding to fragmentation of furfuraldehyde thiosemicarbazone, which loses a $[N_2]^{+\cdot}$ m/z = 27 forming the species 139 $[C_6H_7SNO]^{+\cdot}$; 81 $[C_5H_5O]^{+\cdot}$; 65 $[C_4HO]^{+\cdot}$; 26 $[CO]^{+\cdot}$; 39 $[C_3H_3]$ which may be take two hydrogen radicals forming $[C_3H_5]^{+\cdot}$ with m/z = 41. The other branch (b) includes the fragments $[C_3H_7]^{+\cdot}$ with m/z = 43 and $[(OH)_2PS_2H]^{+\cdot}$ with m/z = 131 (100%) which forms $[PS_2]^{+\cdot}$ radical m/z = 95.



SCHEME 2

Thermal Data of the Complexes

Thermogravimetric studies were carried out on a number of the prepared complexes. The data of these studies are presented in Table IV from the TG-DTG curves. The thermal behavior of the complexes is described as follows:

i) The TGA thermograms of the type [Ni{(RO)$_2$PS$_2$}$_2$Tsc] consist of number of stages. The first mass loss of the complex [Ni{CH$_3$O)$_2$PS$_2$}$_2$Tsc] occurs at 248°C which agrees with elimination of Tsc molecule (found 20.3%, calc. 19.4), while this step was showed at 198°C for [Ni{(EtO)$_2$PS$_2$}$_2$Tsc] and the mass loss correspond to evolution of Tsc + CH$_2$=CH$_2$ molecules

TABLE IV TG and DTG Data of the Complexes

Compound	Step	Temp. range	Max. temp. °C	Mass loss % % (calc.)
$\mathrm{Ni\{(MeO)_2PS_2\}_2Tsc}$	First	0–250	248	20.2 (19.4)
	Second	350–580	426	33.8
	residue	—	687	39.8 (39.7)
$\mathrm{[Ni\{(EtO)_2PS_2\}_2Tsc]}$	First	0–240	198	21.7 (23.0)
	Second	250–300	277	5.2 (5.4)
	Third	300–350	324	13.3
	residue	—	660	30.1 (30.8)
$\mathrm{[Ni\{(PropO)_2PS_2\}_2Tsc]}$	First	0–17	139	4.3
	Second	175–265	233	38.1
	Third	265–450	274	19.6
	residue	—	580	28.4 (27.4)
$\mathrm{[Ni\{(EtO)_2PS_2\}_2ApTsc]}$	First	30–240	179	17.9
	Second	240–390	265	20.6
	residue	—	680	28.3 (27.2)
$\mathrm{[Ni\{(MeO)_2PS_2\}_2ApTsc]}$	First	30–250	215	29.8
	Second	250–310	259	11.6
	residue			
$\mathrm{[Ni\{(MeO)_2PS_2\}FrTsc \cdot 2H_2O]}$	First	90–150	131	12.3
	Second	150–275	207	26.4
	residue		700	36.8 (36.1)
$\mathrm{[Ni\{(EtO)_2PS_2\}FrTsc \cdot 2H_2O]}$	First	0–325	207	42.5
	Second	325–550	429	16.5
	residue	—	666	34.9 (34.8)
$\mathrm{[Ni\{(PropO)_2PS_2\}FrTsc \cdot 2H_2O]}$	First	0–230	200	23.6
	Second	230–270	233	19.4
	residue	—	700	31.7 (31.9)

(found 21.7%, calc. 23.0%). The thermal behavior of the complex $\mathrm{[Ni\{(PropO)_2PS_2\}_2Tsc]}$ (Figure 3) exhibits a number of peaks in (DTG) at 139, 233, 274, and 580°C, unfortunately it was difficult to identify the mass loss of each step. The final product of all the compounds is $\mathrm{NiSO_4}$.

ii) The first mass loss of the two complexes $\mathrm{[Ni\{(MeO)_2PS_2\}_2ApTsc]}$ and $\mathrm{[Ni\{(EtO)_2PS_2\}_2ApTsc]}$ is in agreement with the elimination of $\mathrm{C_7H_7N]}$ from the first complex (found 17.9%, calc. 18.4%) and ApTsc molecule from the second compound (found 31.20%, calc. 29.8%). The unstable complex in each case decomposes and form $\mathrm{NiSO_4}$ as a final product.

iii) The first and second steps of TG and DTG thermograms of the two complexes $\mathrm{[Ni\{(EtO)_2PS_2\}(FrTsc) \cdot 2H_2O]}$ (Figure 4) and $\mathrm{[Ni\{(PropO)_2PS_2\}\ (FrTsc) \cdot 2H_2O]}$ are composite at 207, 409°C and 200, 233°C respectively. It corresponds to the mass loss of

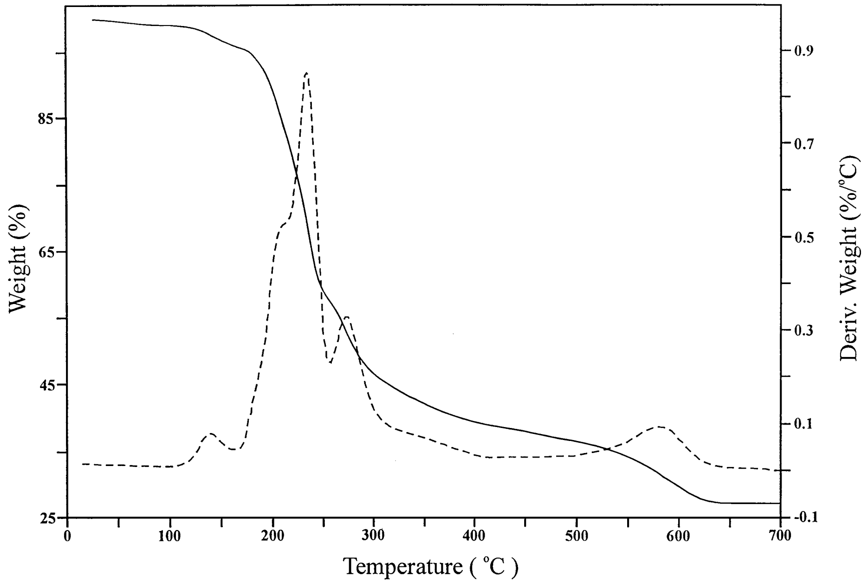


FIGURE 3 TG (——) and DTG (- - -) thermograms of $[Ni\{(PropO)_2PS_2\}_2\ Tsc]$.

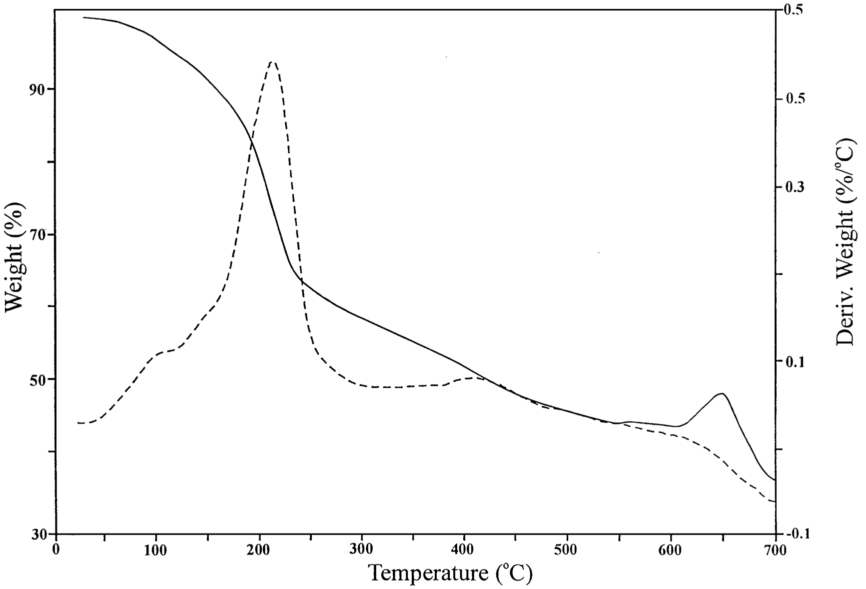


FIGURE 4 TG (——) and DTG (- - -) thermograms of $[Ni\{(EtO)_2PS_2\}_2FurTsc \cdot 2H_2O]$.

TABLE V Antimicrobial Data for Some Complexes

	Fungi				Bacteria		
Compound	*A. Fumig. var. albus*	*A. niger*	*C. tropicum*	*F. oxysporium*	*B. cereus*	*St. aureus*	*P. aeruginosa*
$[Ni\{(EtO)_2PS_2\}_2Tsc]$	8	—	—	—	12	10	—
$[Ni\{(EtO)_2PS_2\}_2ApTsc]$	15	15	15	20	22	0	10
$[Ni\{(EtO)_2PS_2\}FurTsc \cdot 2H_2O]$	12	10	12	10	13	15	17
Erythromycine	0	0	0	0	0	0	0

The diameter of the inhibition zone (in mm).

$FurTsc+2H_2O+2C_2H_4$ (found 59.03, calc. 58.68) in the first compound. For the second compound, the mass losses is a good agreement with elimination of ($FurTsc+2H_2O$) (found 43.0, calc. 43.8%). Elimination of alkenes from alkylthiophosphate was recorded in literature.[21] Three DTG peaks at 131, 207, and 700°C are observed in the thermogram of $[Ni\{(MeO)_2PS_2\}FurTsc \cdot 2H_2O]$ compound and we can not identify the mass losses of each step. The final product of all complexes of this type is $NiSO_4$.

ANTIMICROBIAL ACTIVITY

Representative complexes were screened for their antibacterial activity against different three species of bacteria, gram positive *Bacillus cereus,* gram positive *St. aureas* and *P. aeruginosa*, and four species of fungi, *A. fumig. var. allous*, *A. niger*, *C. tropicum*, and *F. oxysporium* using the filter paper technique[40] measuring the zone of inhibition in mm at 500 $\mu g \cdot ml^{-1}$ concentration. The screening results are summarized in Table V and indicate that among of the tested compounds $[Ni\{(EtO)_2PS_2\}_2ApTsc]$ showed good growth inhibition against all the bacteria and fungi. This may be attributed to the pyridyl ring of 2-acetyl pyridine.[21] Moreover, it shows a high degree of activity if compared with the related complexes[21] (2-acetylpyridinesemicarbazone) may be due to sulphur atom in this type of the complexes.

REFERENCES

[1] M. J. M. Campbell, *Coord. Chem. Rev.*, **15,** 279 (1975).

[2] D. X. West, S. B. Padhye, and P. B. Sopawane, *Structure and Bonding* (Springer, Berlin, 1991), vol. 76, p. 1.

[3] S. Padhye and G. B. Kauffman, *Coord. Chem. Rev.*, **63,** 127 (1985).

[4] T. I. Malinovskii, Yu. A. Simonov, N. V. Gerbeleu, et al., *Problemi Kristallokhimii* (Nauka, Moskva, 1985), p. 3.

[5] Y. Kang, N. Yang, S. O. Kang, and J. Ko, *Organometallics*, **16,** 5522 (1997).

[6] D. X. West, J. K. Swearingen, J. V. Martinez, et al., *Polyhedron*, **18,** 2919 (1999).

[7] P. Tarasconi, S. Capacchi, G. Pelosi, et al., *Bioorgan. Med. Chem.*, **8,** 157 (2000).

[8] L. J. Ackerman, P. E. Franwick, M. A. Green, et al., *Polyhedron*, **18,** 2759 (1999).

[9] S. Teoh, S. Ang, H. Fun, and C. Ong, *J. Organomet. Chem.*, **17,** 580 (1999).

[10] E. Bermejo, R. Carballo, A. Castineiras, et al., *Polyhedron*, **18,** 3695 (1999).

[11] S. Abram, C. M. Mssmer, and U. Abram, *Polyhedron*, **17,** 131 (1998).

[12] D. R. Williams, *Chem. Rev.*, **72,** 203 (1972).

[13] A. Furst and R. T. Haro, *Progr. Exp. Tumor Res.*, **12,** 102 (1969).

[14] F. P. Dwyer, E. M. F. Roe, and A. Shulman, *Brit. J. Cancer*, **19,** 195 (1965).

[15] S. Chandra, L. Gupta, and V. P. Tyagi, *Synth. React. Inorg. Met-Org. Chem.*, **26,** 125 (1996).

[16] R. C. Olivares, R. A. Toscano, C. Silvestru, et al., *J. Organomet. Chem.*, **493,** 61 (1995).

[17] A. I. El-Said, A. S. A. Zidan, M. S. El-Meligy, A. A. M. Ali, and O. F. Mohammed, *Transition Met. Chem.*, **26,** 13 (2001).

[18] D. B. Sowerby, I. Haiduc, A. B. Rusu, and M. Salajan, *Inorg. Chim. Acta*, **68,** 87 (1983).

[19] C. Silvestu, M. Curtui, I. Haiduc, M. J. Begley, and D. B. Sowerby, *J. Organomet. Chem.*, **426,** 49 (1992).

[20] A. A. M. Aly, M. S. El-Meligy, A. S. A. Zidan, and M. El-Shabasy, *Synth. React. Inorg. Met-Org. Chem.*, **17**(3), 257–274 (1987).

[21] A. S. A. Zidan, *Phosphours, Sulphur and Silicon*, **178,** 1–15 (2003).

[22] K. A. Rufenacht, *Chim. Acta*, **51,** 518 (1968).

[23] H. L. Singh, M. Sharma, and A. K. Varshney, *Synth. React. Inorg. Met-Org. Chem.*, **29**(5), 817–826 (1999).

[24] N. K. Singh and R. Tripathi, *Transition Met. Chem.*, **13,** 346 (1988).

[25] K. M. Ibrahim and M. M. Bekkeit, *Transition Met. Chem.*, **13,** 230 (1988).

[26] A. A. El-Asmy, Y. M. Shaibi, I. M. Shedaiwa, and M. A. Khattab, *Synth. React. Inorg. Met-Org. Chem.*, **20,** 461 (1990).

[27] G. R. Burns, *Inorg. Chem.*, **7,** 277 (1968).

[28] S. Chendra and K. K. Sharma, *Synth. React. Inorg. Met-Org. Chem.*, **12,** 123 (1982).

[29] D. X. West, R. M. Makeever, J. P. Scevill, and D. L. Klayman, *Polyhedron*, **3,** 947 (1984).

[30] C. K. Alphonsa and M. R. P. Kurup, *Synth. React. Inorg. Met-Org. Chem.*, **29,** 805–815 (1999).

[31] M. E. Khalifa, T. H. Rakha, and M. M. Bekheit, *Synth. React. Inorg. Met-Org. Chem.*, **26,** 1149 (1996).

[32] A. A. El-Asmy, H. E. Mabrouk, T. Y. Al-Ansi, R. R. Amin, and M. F. El-Shahat, *Synth. React. Inorg. Met-Org. Chem.*, **23,** 1709 (1993).

[33] S. H. Abo El-Fetoh, A. E. Eid, A. I. Abo El-Kareem, and M. A. Wassel, *Synth. React. Inorg. Met-Org. Chem.*, **30,** 513–532 (2000).

[34] B. T. Khan and S. M. Zakeeruddin, *Transition Met. Chem.*, **16,** 119 (1991).

[35] P. Bindu, M. P. Kurup, and T. Satyakeerty, *Polyhedron*, **18,** 321 (1999).

[36] J. El-Mostapha, R. Amedee, A. Magali, K. A. Mustayeen, and B. M. Gilles, *Polyhedron,* **20,** 67 (2001).

[37] H. W. Roesky, *Z. Naturforsch*, **23b,** 103 (1968).

[38] S. Chandra and R. Singh, *Synth. React. Inorg. Met-Org. Chem.*, **17,** 869 (1987).

[39] K. Balakrishman and K. K. Aravindakshan, *J. Indian Chem. Soc.*, **65,** 187 (1991).

[40] N. Kalyoncuoglu, S. Rollas, D. Sur-Attiner, Y. Yegenoglu, and O. Ang, *Pharmazie*, **47,** 769 (1992).