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## Synthesis and Characterization of some Transition Metal Complexes of Thiosemicarbazones Derived from 2-acetylpyrrole and 2-acetylfuran

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## Synthesis and Characterization of some Transition Metal Complexes of Thiosemicarbazones Derived from 2-acetylpyrrole and 2-acetylfuran

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Copper(II), nickel(II), palladium(II), platinum(II), and silver(I) complexes of 2-acetylpyrrole thiosemicarbazone  $(H_2L^1)$  and copper(II), nickel(II), platinum(II) and zinc(II) complexes of 2-acetylfuran thiosemicarbazone  $(HL^2)$  have been prepared and characterized by conductance, electronic, infrared, magnetic and <sup>1</sup>H NMR spectral measurements in addition to elemental and thermogravimetrical analyses. Square-planar structures are suggested for the  $H_2L^1$  complexes of Cu(II), Ni(II), Pd(II) and Pt(II), whereas octahedral structures proposed for the  $HL^2$  complexes of Cu(II) and Ni(II); the Zn(II) and Ag(I) complexes are tetrahedral. Moreover, the results showed that the ligand  $H_2L^1$  is bidentate in all of its complexes, and the ligand  $HL^2$  is either mono-, di- or tridentate.

Keywords Z-acetylpyrrole, Z-acetylfuran, thiosemicarbazones, transition metal complexes

#### INTRODUCTION

Thiosemicarbazone derivatives and their metal complexes have extensive biological properties such as antitumor (Belicchi et al., 1999; Kovala-Demertzi et al., 1997; Kovala-Demertzi et al., 2001; Quiroga et al., 1999; Tarasconi et al., 2000), fungicidal (Bermejo et al., 1999; Jouad et al., 2001a), bactericidal (Bindu et al., 1999), and antiviral (Tarasconi et al., 2000) activity. We have previously described the complexes formed between chromone thiosemicarbazones and some transition metal ions (Youssef et al., 2003). We report here the synthesis and the characterization of complexes of 2-acetylpyrrole thiosemicarbazone with Cu(II), Ni(II), Pd(II), Pt(II), and Ag(I) ions and those of 2-acetylfuran thiosemicarbazone with Cu(II), Ni(II), Pt(II) and Zn(II) ions.

#### **EXPERIMENTAL**

#### Synthesis of the Ligands

The ligands  $H_2L^1$  and  $HL^2$  (Figure 1) were prepared by mixing 1.82 g (20 mmol) of thiosemicarbzide with 2.18 g (20 mmol) of 2-acetylpyrrole or 2.20 g (20 mmol) of 2-acetylfuran in 150 mL of methanol. The mixtures were then stirred for 12 and 1/2 h, in case of ligands  $H_2L^1$  and  $HL^2$ , respectively, when the solid ligands precipitated. The solids were filtered, washed with methanol, and finally dried in a vacuum desiccator over anhydrous CaCl<sub>2</sub>. The yields were 2.54 g (69.78%) and 3.21 g (87.70%) for the ligands  $H_2L^1$  and  $HL^2$ , respectively.

#### Synthesis of the Metal Complexes

The complexes  $[Ni(H_2L^1)Cl_2] \cdot H_2O$ ,  $[Ni(L^2)(H_2O)_2 Cl] \cdot 3H_2O$ ,  $[Ag(H_2L^1)(H_2O)NO_3] \cdot 2H_2O$  and  $[Cu(HL^2)(H_2O)Cl_2] \cdot H_2O$  were prepared by mixing an aqueous solution (10 mL) of the metal salt (2.5 mmol of NiCl\_2 \cdot 6H\_2O, AgNO\_3 or CuCl\_2 \cdot 2H\_2O, respectively) with a warm methanol solution (~40°C) (50 mL) of the ligands  $H_2L^1$  or  $HL^2$  (2.5 mmol). The  $[Pt(H_2L^1)Cl_2] \cdot 4H_2O$  complex was prepared by the same method using an aqueous solution (20 mL) of platinum(II) chloride (0.8 mmol) and methanol solution (~40°C) (20 mL) of the ligand  $H_2L^1$  (0.8 mmol).

The complexes  $[Cu(H_2L^1)_2]Cl_2 \cdot 5H_2O$  and  $[Zn(HL^2)_2Cl_2]$ were synthesized by mixing an aqueous solution (10 mL) of the metal salt (2.5 mmol of CuCl<sub>2</sub> · 2H<sub>2</sub>O or ZnCl<sub>2</sub>, respectively) with a warm methanol solution (~40°C) (50 mL) of the ligands  $H_2L^1$  or HL<sup>2</sup> (5 mmol). The complexes  $[Pd(H_2L^1)_2]Cl_2 \cdot 2H_2O$ and  $[Pt(L^2)_2]$  were prepared by the same method using aqueous solutions (20 mL) of palladium chloride or platinum(II) chloride (0.8 mmol) and methanol solution (~40°C) (50 mL) of the ligands  $H_2L^1$  or HL<sup>2</sup> (1.6 mmol).

For the Pd(II) and Pt(II) compounds, stock solutions of  $0.04 \text{ M} [PdCl_4]^{2-}$  and  $[PtCl_4]^{2-}$  were first prepared following the procedure described in the literature (Kovala-Demertzi et al., 2000).

The reaction mixture was then gently refluxed with constant stirring for a time depending on the transition metal salt used.

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FIG. 1. Structure of the ligands.

The resulting precipitates were filtered, washed with methanol, then with diethyl ether, and dried over anhydrous CaCl<sub>2</sub>.

#### **Physical Measurements**

The ligands and their complexes were analyzed for C, H, N, S, Cl, and M contents at the Microanalytical Laboratory, Faculty of Science, Cairo University, Egypt. The metal ion contents of the complexes were also determined (Holzbecher et al., 1976; Vogel, 1978; Welcher, 1958) by previously reported methods (McDonald and Sirichanva, 1969; Youssef, 2000). IR spectra of the ligands and their metal complexes were measured using KBr discs with a Jasco FT/IR 300E Fourier transform infrared spectrophotometer covering the range  $400-4000 \,\mathrm{cm}^{-1}$  and in the  $500-100 \,\mathrm{cm}^{-1}$  region using polyethylene-sandwiched Nujol mulls on a Perkin Elmer FT-IR 1650 spectrophotometer. <sup>1</sup>H NMR spectra of the ligands and some of their complexes were recorded in DMSO-d<sub>6</sub> using a Jeol EX-270 MHz NMR spectrophotometer from 0-14 ppm with TMS as an internal standard. The electronic spectra of the ligands and their complexes were obtained in Nujol mulls and in saturated DMF or DMSO solutions using a Shimadzu UV-240 UV-visible recording spectrophotometer. Thermogravimetric analyses of the investigated complexes were carried out using DTA-7 and TGA-7 Perkin Elmer 7 series thermal analysis systems. The mass losses were measured in nitrogen atmosphere from ambient temperature up to  $800^{\circ}$ C at a heating rate of  $10^{\circ}$ C min<sup>-1</sup>. Molar conductivities in DMF or DMSO at 25°C were measured using a model CM-1K-TOA Company (Japan) conductivity meter. Magnetic moments at 25°C were determined using the Gouy method with Hg[Co(SCN)<sub>4</sub>] as calibrant.

#### **RESULTS AND DISCUSSION**

The formation of the metal chelates of the ligands  $H_2L^1$  and  $HL^2$  is expressed by the following chemical equations:

$$MCl_2 + H_2L^1 \xrightarrow{aqueous-methanol} [M(H_2L^1)Cl_2] \cdot nH_2O$$
$$M = Ni(II), (n = 1);$$
$$Pt(II), (n = 4)$$

$$\begin{array}{c} \mathrm{MCl}_{2} + 2\mathrm{H}_{2}\mathrm{L}^{1} & \xrightarrow{\mathrm{aqueous-methanol}} & [\mathrm{M}(\mathrm{H}_{2}\mathrm{L}^{1})_{2}]\mathrm{Cl}_{2} \cdot \mathrm{xH}_{2}\mathrm{O} \\ & \mathrm{M} = \mathrm{Cu}(\mathrm{II}), (\mathrm{x} = 5); \\ & \mathrm{Pd}(\mathrm{II}), (\mathrm{x} = 2) \end{array}$$

$$\begin{array}{c} \mathrm{AgNO}_{3} + \mathrm{H}_{2}\mathrm{L}^{1} & \xrightarrow{\mathrm{aqueous-methanol}} & [\mathrm{Ag}(\mathrm{H}_{2}\mathrm{L}^{1})(\mathrm{H}_{2}\mathrm{O})\mathrm{NO}_{3}] \\ & \cdot 2\mathrm{H}_{2}\mathrm{O} \end{array}$$

$$\begin{array}{c} \mathrm{CuCl}_{2} + \mathrm{HL}^{2} & \xrightarrow{\mathrm{aqueous-methanol}} & [\mathrm{Cu}(\mathrm{HL}^{2})(\mathrm{H}_{2}\mathrm{O})\mathrm{Cl}_{2}] \cdot \mathrm{H}_{2}\mathrm{O} \end{array}$$

$$\begin{array}{c} \mathrm{NiCl}_{2} + \mathrm{HL}^{2} & \xrightarrow{\mathrm{aqueous-methanol}} & [\mathrm{Ni}(\mathrm{L}^{2})(\mathrm{H}_{2}\mathrm{O})_{2}\mathrm{Cl}] \cdot 3\mathrm{H}_{2}\mathrm{O} \\ & + \mathrm{HCl} \end{array}$$

$$\begin{array}{c} \mathrm{ZnCl}_{2} + 2\mathrm{HL}^{2} & \xrightarrow{\mathrm{aqueous-methanol}} & [\mathrm{Zn}(\mathrm{HL}^{2})_{2}\mathrm{Cl}_{2}] \end{array}$$

$$\begin{array}{c} \mathrm{PtCl}_{2} + 2\mathrm{HL}^{2} & \xrightarrow{\mathrm{aqueous-methanol}} & [\mathrm{Pt}(\mathrm{L}^{2})_{2}] + 2\mathrm{HCl} \end{array}$$

The elemental and, in some cases, the thermogravimetric analyses of the ligands and the solid complexes, listed in Tables 1 and 2, showed that the stoichiometry of the complexes obtained is 1:1 and 1:2 (metal:ligand) for both of the two ligands  $H_2L^1$  and  $HL^2$ .

#### **Infrared Spectra**

The significant IR bands of the ligands and their metal complexes and their assignments are given in Table 3. The absence of bands in the  $2000-2500 \text{ cm}^{-1}$  region (Carballo et al., 2001) due to  $\nu$ (S–H) in most spectra of the complexes suggests that these ligands exist mainly in the thione form. However, the spectrum of  $[Cu(HL^2)(H_2O)Cl_2] \cdot H_2O$  exhibits a  $\nu(S-H)$ band at  $2120 \,\mathrm{cm}^{-1}$ , which is a good evidence that the ligand HL<sup>2</sup> readily converts to the thiol form, without deprotonation, on coordination with the Cu(II) ion. The bands due to  $\nu$ (CS) and  $\nu(CS) + \nu(CN)$  at 750–920 and 1280–1390 cm<sup>-1</sup>, respectively, in the free ligands  $H_2L^1$  and  $HL^2$  are either shifted, split, or disappeared in all of their complexes, indicating the participation of the S atom in complex formation (John et al., 2002). The presence of a new band due to  $\nu$  (M-S) (Fostiak et al., 2002) at  $300-408 \text{ cm}^{-1}$  in the H<sub>2</sub>L<sup>1</sup> and HL<sup>2</sup> complexes is another indication of the involvement of the S atom in coordination. Moreover, coordination of the azomethine N to the metal ion is suggested by the shift of the  $\nu$  (C=N) band (Kovala-Demertzi et al., 2001) and the occurrence of the  $\nu(N-N)$  band at higher wave numbers in all of the studied complexes except for the  $[Zn(HL^2)_2Cl_2]$  complex. Coordination of the azomethine N is also consistent with the presence of a band at 332-412 and 560-600 cm<sup>-1</sup> in case of  $H_2L^1$  and  $HL^2$  complexes, respectively, except for the  $[Cu(HL^2)(H_2O)Cl_2] \cdot H_2O$  complex, which are assignable to  $\nu$ (M–N) for these complexes (West et al., 1995).

The significant displacement of the frequency of the furan ring breathing and  $\nu(C-O-C)$  vibrations (Jouad et al., 2002) in case of the  $[Ni(L^2)(H_2O)_2Cl] \cdot 3H_2O$  and  $[Cu(HL^2)(H_2O)Cl_2] \cdot H_2O$  complexes is explicit evidence for the

				M.p.	Analysis (%)/found (calcd.)				Molar		
Complexes	FW	Yield (%)	Color	(D.p.) (°C)	С	Н	Ν	S	CI	М	conductance $\Lambda_{\rm m}  (\Omega^{-1}  {\rm cm}^2  {\rm mol}^{-1})$
Ligand H <sub>2</sub> L <sup>1</sup> C <sub>7</sub> H <sub>10</sub> N <sub>4</sub> S	182	70	Reddish	213	45.90	5.62	29.97	18.17			
Ligand HL <sup>2</sup> C <sub>7</sub> H <sub>9</sub> N <sub>3</sub> OS	183	88	brown Dark	(160–165)	(46.15) 45.52	(5.49) 4.77	(30.77) 22.73	(17.58) 17.64			
$[Cu(H_2L_1)_2]Cl_2 \cdot 5H_2O$	588.55	79	yellow Brown	170-180	(45.90) 28.17	(4.92) 5.10	(22.29) 19.21	(17.49) 10.65	11.90	11.13	85.0
$\begin{bmatrix} C_{14}H_{30}Cl_2CuN_8O_5S_2\\ [Ni(H_2L^1)Cl_2] \cdot H_2O \end{bmatrix}$	329.69	77	Brown	170	(28.54) 25.39	(5.10) 3.78	(19.03) 17.13	(10.87) 9.85	(12.06) 21.21	(10.80) 17.97	8.7
$[Pd(H_2L^1)_2]Cl_2 \cdot 2H_2O$	577.40	85	Reddish	260-270	(25.48) 29.41	(3.64) 4.00	(16.98) 19.63	(9.71) 10.82	(21.54) 12.45	(17.80) 18.27	75.8
$C_{14}H_{24}Cl_2N_8O_2PdS_2$ [Pt(H <sub>2</sub> L <sup>1</sup> )Cl <sub>2</sub> ] · 4H <sub>2</sub> O	520.08	90	brown Brown	240-250	(29.09) 16.21	(4.16) 3.51	(19.40) 10.60	(11.08) 6.12	(12.30) 13.43	(18.43) 37.42	14.2
$\begin{array}{l} C_7H_{18}Cl_2N_4O_4PtS\\ [Ag(H_2L^1)(H_2O)NO_3]\cdot 2H_2O\end{array}$	405.87	82	Grey	170-180	(16.15) 20.61	(3.46) 3.98	(10.77) 17.51	(6.15) 8.02	(13.65)	(37.51) 26.17	36.0
$\begin{array}{c} C_7H_{16}AgN_5O_6S\\ [Zn(HL^2)_2Cl_2] \cdot \end{array}$	502.39	80	Buff	223	(20.70) 32.94	(3.94) 3.62	(17.25) 16.81	(7.88) 12.85	13.87	(26.58) 13.25	8.2
$C_{14}H_{18}Cl_2N_6O_2S_2Zn$ [Pt(L <sup>2</sup> ) <sub>2</sub> ]	559.08	89	Dark green	260-270	(33.44) 29.69	(3.58) 2.92	(16.72) 15.31	(12.74) 11.34	(14.13)	(13.02) 35.33	20.8
$C_{14}H_{16}N_6O_2PtS_2$ [Ni(L <sup>2</sup> )(H <sub>2</sub> O) <sub>2</sub> C]] · 3H <sub>2</sub> O	366.19	78	Green	228	(30.05) 23.10	(2.86) 5.04	(15.02) 11.65	(11.45) 8.38	9.52	(34.89) 16.33	7.7
$C_7H_{18}CIN_3NiO_6S$	252 55	71	Brownish	160 170	(22.94)	(4.92)	(11.47)	(8.74)	(9.69)	(16.03)	16.3
$C_7H_{13}Cl_2CuN_3O_3S$	555.55	/1	red	100-170	(23.76)	(3.68)	(11.88)	(9.05)	(20.08)	(17.97)	10.5

TABLE 1 Analytical and physical data of the ligands  $H_2 L^1$  and  $HL^2$  and their metal complexes

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			Water e					
	M:L	Hydrated water mass loss %		Coordinated water mass loss %		Other	Residue (%)	
Complex		Temp. (°C)	Found (calcd.)	Temp. (°C)	Found (calcd.)	Other decomposition stages (°C)	Temp. (°C)	Found (calcd.)
$[Cu(H_2L^1)_2Cl_2]\cdot 5H_2O$	1:2	115	15.51 (15.29)	_	_	160-201 201-490 490-607	607	13.61 (13.52) Cu <sub>2</sub> S
$[Ni(H_2L^1)Cl_2] \cdot H_2O$	1:1	102	5.57 (5.46)	—	_	180–240 240–350 350–758 233–425	758	22.92 (24.27) Ni <sub>3</sub> S <sub>2</sub>
$[Pt(H_2L^1)Cl_2]\cdot 4H_2O$	1:1	114	13.58 (13.84)	—	_	425-518	518	43.10 (43.66) PtS
$[Ag(H_2L^1)(H_2O)NO_3] \cdot 2H_2O$	1:1	110	9.03 (8.87)	—	—	120-245 245-604 604-707	707	27.01 (26.60) Ag
$[\mathrm{Ni}(\mathrm{L}^2)(\mathrm{H}_2\mathrm{O})_2\mathrm{Cl}]\cdot 3\mathrm{H}_2\mathrm{O}$	1:1	120	14.89 (14.75)	150-215	10.07 (9.83)	215-250 250-536 536-760	760	21.43 (20.40) NiO
$[Cu(HL^2)(H_2O)Cl_2] \cdot H_2O$	1:1	103	4.76 (5.09)	_	_	113-200 200-434 434-718	718	23.39 (22.50) CuO

	TABLE 2		
ermogravimetric analysis results of the	ne investigated metal co	omplexes of the li	gands H <sub>2</sub> L <sup>1</sup> and HL <sup>2</sup>

coordination of the ligand  $HL^2$  through the furan oxygen atom (Jouad et al., 2001b). This is supported by the presence of the  $\nu$ (M–O) vibration (Jouad et al., 2001) at 428–435 cm<sup>-1</sup>.

The presence of  $\nu$ (C==N),  $\nu$ (furan ring) and  $\nu$ (C-O-C) in case of the  $[Zn(HL^2)_2Cl_2]$  complex at the same position as those in the uncomplexed ligand, together with the  $\nu$ (N-H) shift to higher wave number and the absence of any band due to M-O and M-N stretching vibrations, are consistent with nondeprotonation and the sole coordination through the sulfur atom (Castineiras et al., 2001).

The molar conductance of  $[Ag(H_2L^1)(H_2O)NO_3]\cdot 2H_2O$ complex in DMF is  $36.0 \,\Omega^{-1} \,\mathrm{cm}^2 \,\mathrm{mol}^{-1}$ , which indicates that the ligand  $H_2L^1$  is coordinated to the Ag(I) ion as non-deprotonated chelating agent and that the nitrate ion is also coordinated to the silver ion (Ali et al., 1996), which may also be supported by the band observed at  $1320 \text{ cm}^{-1}$  due to a coordinated nitrate group (Bellamy, 1978). The coordination of the nitrate group has been ascertained by the band at 321 cm<sup>-1</sup>, which may be reasonably assigned to  $\nu(M-O)$  of the O-NO<sub>2</sub> group (Shakir et al., 2003).

#### <sup>1</sup>H NMR Spectra

The <sup>1</sup>H NMR spectra of the ligands  $H_2L^1$  and  $HL^2$  and their diamagnetic complexes in DMSO solutions with assignments are collected in Table 4. The <sup>1</sup>H NMR spectra of the free ligands showed exchangeable singlets assigned to the imino proton and the amino protons at 10.03-10.38 and 8.09-8.49 ppm, respectively. These signals disappeared in the presence of  $D_2O$ .

	-						-		-			
Compound	ν(NH <sub>2</sub> )	v(NH)	$\nu$ (C=N) + $\nu$ (C-C)	v(ring)	v(C-O-C)	$\nu(N-N)$	$\nu$ (C=S) + $\nu$ (C-N)	$\nu(C=S)$	ν(M-N)	ν(M-O)	$\nu(M-S)$	$\nu(S-H)$
Ligand H <sub>2</sub> L <sup>1</sup>	3480 m 3420 m	3360 m 3240 m 3180 m	1640 m 1590 s 1520 s	1515 s		1035 s	1280 s	830 s 750 s				
$[Cu(H_2L^1)_2Cl_2]\cdot 5H_2O$	3400-	-3200 b	1620 s 1540 m	1520 w		1045 s	1260 m	820 w 770 w	412 w 389 m		311 m	
$[Ni(H_2L^1)Cl_2] \cdot H_2O$	3480– 3400 w	3360 m 3240 m	1640 s 1600 m	1515 s		1050 s	1235 s	820 m 750 s 700 s	332 b		301 m	
$[Pd(H_2L^1)_2]Cl_2\cdot 2H_2O$	3540 w 3440 b	3360 m 3180 m	1600 s 1560 s 1540 m	1520 w		1050 s	1305 s 1205 m 1170 s	770 s 730 s	403 s		300 m	
$[Pt(H_2L^1)Cl_2]\cdot 4H_2O$	3600- 3560 b	3440 b 3360 b 3280 b	1600 m 1560 m	1520 s		1040 s	1310 w 1270 m	820 m 740 s 680 m	348 m		300 m	
$[Ag(H_2L^1)(H_2O)NO_3]\cdot 2H_2O$	3560 b	3360 b 3280 w 3180 w	1620 m 1570 s	1520 m		1045 s	_	815 s 730 s 695 m	368 m	321 w	300 s	
Ligand HL <sup>2</sup>	3600 s 3480 s	3380– 3140 m	1590 s	1020 s	1290 m	1100 s	1390 m	920 s 840 s				
$[Zn(HL^2)_2Cl_2]$	3500 b	3300 m 3220 w	1590 s	1020 s	1285 b	1090 w	1370 w	820 w	—		344 s	
$[Pt(L^2)_2]$	3560 b	3360 m 3220 w 3100 b	1640 s 1600 s	1020 m	1300 s	1130 s	_	930 s	560 s	—	362 s	
$[\mathrm{Ni}(\mathrm{L}^2)(\mathrm{H}_2\mathrm{O})_2\mathrm{Cl}]\cdot 3\mathrm{H}_2\mathrm{O}$	3380 b	3260 m 3080 m	1640 s 1610 s 1570 w	1000 m	1235 s	1150 m	1440 s 1390 s 1350 s	790 s 700 s	600 s	435 m	408 m	
$[Cu(HL^2)(H_2O)Cl_2] \cdot H_2O$	3480 b	3260 m 3000 b	1630 s 1600 s	1010 w	1190 s	1140 s	—	_	600 s	428 m	340 m	2120 s

TABLE 3 IR frequencies of the bands  $(cm^{-1})$  of  $H_2L^1$  and  $HL^2$  ligands and their complexes and their assignments

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TABLE 4 <sup>1</sup>H NMR spectral data of the ligands  $H_2L^1$  and  $HL^2$  and their diamagnetic Ni(II), Pd(II), Pt(II), Ag(I) and Zn(II) complexes recorded in DMSO-d<sub>6</sub> solution

		nents		
Ligands and their Complexes	Acetyl CH <sub>3</sub>	CS-NH <sub>2</sub>	CS-NH	N(1)H (Pyrrole)
Ligand H <sub>2</sub> L <sup>1</sup>	2.50	8.26	10.03	11.30
$[Ni(H_2L^1)Cl_2] \cdot H_2O$	2.58	8.13 8.28	9.83	11.39
$[Pd(H_2L^1)_2]Cl_2\cdot 2H_2O$	2.35	8.19 8.64	10.50	10.95
$[Ag(H_2L^1)(H_2O)NO_3] \cdot 2H_2O$	2.54	8.16 8.84	10.68	11.47
Ligand HL <sup>2</sup>	2.52	8.82 8.49	10.38	
$[Zn(HL^2)_2]Cl_2$	2.52	8.09 8.26	10.12	
$[Pt(L^2)_2]$	2.58	8.05 7.71	_	
		7.54		

The absence of the imino proton signal in the spectra of the  $[Pt(L^2)_2]$  complex suggests deprotonation of the ligand and possible coordination of the Pt(II) ion to the thiol sulfur (Kovala-Demertzi et al., 2000). The  $[Pt(H_2L^1)Cl_2] \cdot 4H_2O$  complex is insufficiently soluble in DMSO-d<sub>6</sub> to acquire a <sup>1</sup>H NMR spectrum. The signals due to the hydrazinic protons are either shielded or deshielded in case of  $[Ni(H_2L^1)Cl_2] \cdot H_2O$ ,  $[Pd(H_2L^1)_2]Cl_2 \cdot 2H_2O$ ,  $[Ag(H_2L^1)(H_2O)NO_3] \cdot 2H_2O$  and  $[Zn(HL^2)_2Cl_2]$  complexes confirming non-deprotonation and coordination through sulfur atom in these complexes (Carballo et al., 2001).

The <sup>1</sup>H NMR spectra of all  $H_2L^1$  complexes and the  $[Pt(L^2)_2]$  complex show that the acetyl methyl signal is either shifted to higher or lower field on coordination, indicative of variation in the electron density at the C=N group (Kovala-Demertzi et al., 2000). However, no shift of this signal was observed in case of the  $[Zn(HL^2)_2Cl_2]$  spectra, confirming that the azomethine N is not involved in coordination.

The presence of two amino proton signals in the spectra of the  $H_2L^1$  and  $HL^2$  complexes shows magnetic non-equivalence attributable to rotation about the CS–NH<sub>2</sub> bond being impeded by partial double bond character acquired upon S-coordination (Castineiras et al., 2001). It may be also noted that coordination of the ligand  $HL^2$  in the deprotonated form leads to an upfield shift in the NH<sub>2</sub> signals in case of the  $[Pt(L^2)_2]$  spectra (Loabana et al., 1998).

#### **Electronic Spectra and Magnetic Susceptibility**

Listed in Table 5 are the electronic transitions for  $H_2L^1$  and  $HL^2$  and their metal complexes with the magnetic moments of

these complexes. The bands of the free ligands  $H_2L^1$  and  $HL^2$  in the 300–340 nm range are attributable to the imine and thioamide transitions within the thiosemicarbazone moiety.

The observed magnetic moment of the  $[Cu(H_2L^1)_2]Cl_2 \cdot 5H_2O$  complex is 1.75 B.M. The electronic spectrum of this complex shows a shoulder at 500 nm assignable to the  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$  transition overlapped with the S( $\pi$ )  $\rightarrow$  Cu(II) transition (Jasinski et al., 2003; Shakir et al., 1996) and a broad band centered at 380 nm due to the  $S(\sigma) \rightarrow Cu(II)$  transition, suggesting a square-planar geometry around the Cu(II) ion (Jasinski et al., 2003). On the other hand, the  $[Cu(HL^2)(H_2O)]$  $Cl_2$   $\cdot$   $H_2O$  complex has a magnetic moment = 1.85 B.M. and the electronic spectrum of this complex exhibits a broad band centered at 580 nm assigned to the  ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$  transition, indicating a distorted octahedral configuration (Ali et al., 2001).

The electronic spectrum of the diamagnetic  $[Ni(H_2L^1)Cl_2] \cdot H_2O$  complex has a band at 450 nm due to a combination of  ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$  and  $S \rightarrow Ni(II)$  CT transitions and bands at 530 and 600 nm attributable to the  ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ and  ${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$  transitions, consistent with its planar stereochemistry (Fostiak et al., 2002). The magnetic moment of the  $[Ni(L^2)(H_2O)_2Cl] \cdot 3H_2O$  complex is 3.24 B.M., which is typical of high-spin octahedral complexes (Garcia et al., 2002). The electronic spectrum of this complex has absorption bands at 850 and 590–610 nm, assigned to the  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$ and  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$  transitions, respectively, suggesting an octahedral geometry (Fostiak et al., 2002).

A presumably tetrahedral structure is suggested for the diamagnetic  $[Zn(HL^2)_2Cl_2]$  and  $[Ag(H_2L^1)(H_2O)NO_3] \cdot 2H_2O$  complexes (Wu et al., 1999).

Ligands and their complexes	Mode	Intraligand & charge tranfer bands	d–d bands	μ <sub>eff.</sub> (B.M.)
Ligand H <sub>2</sub> L <sup>1</sup>	Nujol	260, 300, 310, 330, 340		
-	DMSO	254 (4.10), 328 (4.22)		
$[Cu(H_2L^1)_2Cl_2] \cdot 5H_2O$	Nujol	240, 290, 320, 380	500 sh	1 75
	DMSO	250 (4.18), 290 (4.23), 330 (4.32)	500 SII	1.75
$[Ni(H_2L^1)Cl_2] \cdot H_2O$	Nujol	240, 275, 340, 360, 385, 450	530, 600	Diamagnetic
	DMSO	330 (4.42)		
$[Pd(H_2L^1)_2]Cl_2 \cdot 2H_2O$	Nujol	230, 260, 325	470	Diamagnetic
	DMSO	280 (4.18), 310 (4.33)	418 (2.38), 590 sh (2.08)	
$[Pt(H_2L^1)Cl_2] \cdot 4H_2O$	Nujol	310, 320, 350, 390	520	Diamagnetic
	DMF	255 (4.15), 335 (4.31)	455 (2.79), 590 sh	
$[Ag(H_2L^1)(H_2O)NO_3] \cdot 2H_2O$	Nujol	220, 360, 380		Diamagnetic
	DMSO	260 (4.25), 330 (4.37), 430 sh		
Ligand HL <sup>2</sup>	Nujol	262, 322		
	DMF	210 (3.91), 249 (3.74), 314 (3.65)		
$[Zn(HL^2)_2]Cl_2$	Nujol	255, 245, 290, 320, 355, 385		Diamagnetic
	DMF	258 (3.98), 320 (3.85), 360 sh		
$[Pt(L^2)_2]$	Nujol	255, 245, 330, 380	450, 510	Diamagnetic
	DMF	209 (3.95), 248 (3.90),	595 (2.54)	
_		316 (4.11), 363 sh		
$[Ni(L^2)(H_2O)_2Cl] \cdot 3H_2O$	Nujol	245, 330, 390, 450 sh	510 sh	3.24
	DMF	270 (4.13)	590 sh (1.90), 610(1.27), 850 sh	
$[Cu(HL^2)(H_2O)Cl_2] \cdot H_2O$	Nujol	250, 310, 320, 330, 380	495 sh	1.85
	DMF	270 (4.02), 330 (3.96)	580 (2.37)	

 TABLE 5

 Electronic absorption spectral bands of the ligands  $H_2L^1$  and  $HL^2$  and their complexes

Numbers in parantheses log  $\epsilon$  ( $\epsilon$ , lit. mol.<sup>-1</sup> cm<sup>-1</sup>).

The electronic spectra of the Pd and Pt complexes are indicative of square-planar geometry. The absorption bands of these complexes at 418–455, 470–520 and 590–595 nm may be assigned to the one-electron transitions  ${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$ ,  ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ , respectively (Kovala-Demertzi et al., 2001).

#### Thermogravimetric Analyses

The thermogravimetric data for the studied complexes are listed in Table 2. The results obtained are in good agreement with the theoretical formulae suggested from the elemental analyses.

The first mass loss from all  $H_2L^1$  and  $HL^2$  complexes in the temperature range of  $102-120^{\circ}$ C, may be due to the loss of hydrated water in these complexes. The mass loss in the temperature range of  $150-215^{\circ}$ C from the  $[Ni(L^2)(H_2O)_2Cl] \cdot 3H_2O$  complex indicates the elimination of coordinated water molecules.

 $\begin{array}{ll} \mbox{The } [Cu(H_2L^1)_2]Cl_2\cdot 5H_2O, \ [Ag(H_2L^1)(H_2O)NO_3]\cdot 2H_2O, \\ [Ni(H_2L^1)Cl_2]\cdot H_2O, \ [Ni(L^2)(H_2O)_2Cl]\cdot 3H_2O \ \ and \end{array}$ 

 $[Cu(HL^2)(H_2O)Cl_2] \cdot H_2O$  complexes have four decomposition steps. These complexes show the first mass loss step, attributed to dehydration, in the temperature range 102 to 120°C. The second decomposition step of these complexes starts around 113-180°C. In case of  $[Ag(H_2L^1)(H_2O)NO_3] \cdot 2H_2O$  and  $[Cu(HL^2)(H_2O)Cl_2] \cdot H_2O$  complexes, abrupt mass losses occur at 120-245 and at 113-200°C, respectively, which may represent the removal of coordinated water associated with the other products of the second decomposition step. The third and the fourth decomposition steps are in the range of 201-604 and 434-760°C, respectively. The fourth step ends with the formation of silver metal in case of the silver complex or the corresponding sulfides, Cu<sub>2</sub>S and Ni<sub>3</sub>S<sub>2</sub> in case of  $[Cu(H_2L^1)_2]Cl_2 \cdot 5H_2O$  and  $[Ni(H_2L^1)Cl_2] \cdot H_2O$ , respectively. In case of the  $[Pt(H_2L^1)Cl_2] \cdot 4H_2O$  complex, there are three decomposition steps. The first mass loss step starts at 114°C, which could be due to the removal of lattice water. The second step starts at 233°C, whereas the third one is in the range 425–518°C and comprises the formation of PtS, followed by decomposition into Pt.



FIG. 2. Suggested structures of the  $H_2L^1$  complexes (M : L = 1 : 1 and 1 : 2).







FIG. 3. Suggested structures of the  $HL^2$  complexes (M : L = 1 : 1 and 1 : 2).

In the case of  $[Ni(L^2)(H_2O)_2Cl] \cdot 3H_2O$  and  $[Cu(HL^2)(H_2O)Cl_2] \cdot H_2O$  complexes, the fourth step ends with the formation of the corresponding oxides: NiO and CuO, respectively.

The amounts of residue are in good agreement with the calculated values.

#### Suggested Structural Formulae of the Complexes

From the spectral data and the elemental and thermal analyses, the structure of the prepared complexes may be formulated as shown in Figures 2 and 3.

#### REFERENCES

- Ali, M. A.; Dey, K. K.; Nazimuddin, M.; Smith, F. A.; Butcher, R. J.; Jasinski, J. P.; Jasinski, J. M. The Preparation and Characterization of Some Copper (II) Complexes of the 6-methyl-2-formylpyridine Thiosemicarbazone and the X-Ray Crystal Structure of the Chloro(6-methyl-2-formylpyridinethiosemicarbazonato)copper(II) Complex. *Polyhedron* 1996, 15, 3331–3339.
- Ali, M. A.; Miraza, A. H.; Hossain, A. M. S.; Nazimuddin, M. Synthesis, Characterization, Antifungal Properties and X-ray Crystal Structures of Five- and Six-Coordinate Cu(II) Complexes of the 6-Methyl-2-formylpyridine <sup>4</sup>N-Dimethylthiosemicarbazone. *Polyhedron* 2001, 20, 1045–1052.
- Belicchi Ferrari, M.; Capacchi, S.; Pelosi, G.; Reffo, G.; Tarasconi, P.; Albertini, R.; Pinelli, S.; Lunghi, P. Synthesis, Structural Characterization and Biological Activity of Helicin Thiosemicarbazone Monohydrate and a Copper(II) Complex of Salicylaldehyde Thiosemicarbazone. *Inorg. Chim. Acta.* **1999**, 286, 134–141.
- Bellamy, L. J. The Infrared Spectra of Complex Molecules; Chapman and Hall: London, 1978.
- Bermejo, E.; Carballo, R.; Castineiras, A.; Dominguez, R.; Liberta, A. E.; Maichle-Mossmer, C.; West, D. X. Complexes of Group 12 Metals with 2-Acetylpyridine <sup>4</sup>N-Dimethylthiosemicarbazone and with 2-Acetylpyride-N-Oxide <sup>4</sup>N-Dimethylthiosemicarbazone. *Synthesis, Structure and Antifungal Activity. Z. Naturforsch.* **1999**, 54b, 777–787.
- Bindu, P.; Kurup, M. P. P.; Satyakeerty, T. R. EPR., Cyclic Voltametric and Biological Activities of Cu(II) Complexes of Salicyladehyde N(4)-Substituted Thiosemicarbazone and Heterocyclic Bases. *Polyhedron* 1999, 18, 321–331.
- Carballo, R.; Castineiras, A.; Perez, T. Group 12 Metal Complexes of 2-Formylpyrrole (4PL<sub>1</sub>) and 2-Acetylpyrrole-N(4)-Phenylthiosemicarbazone (4PL<sub>2</sub>) form Different Donor Modes. Crystal and Molecular Structure of [Hg(4PL<sub>1</sub>-H)Br]<sub>2</sub> and [Zn(4PL<sub>2</sub>)<sub>2</sub>Br<sub>2</sub>] · 2EtOH. Z. Naturforsch. 2001, 56b, 881–888.
- Castineiras, A.; Carballo, R.; Perez, T. Synthesis and Structural Characterization of Complexes of Zn(II), Cd(II) and Hg(II) Halides with 2-formylpyrrole Thiosemicarbazone and 2-acetylpyrrole Thiosemicarbazone. *Polyhedron* **2001**, *20*, 441–448.
- Fostiak, L. M.; Garcia, I.; Sweeringen, J. K.; Bermejo, E.; Castineiras, A.; West, D. X. Structure and Spectral Characterization of Transition Metal Complexes of 2-Pyridineformamide N(4)-Dimethylthiosemicarbazone. *Polyhedron* 2002, 22, 83–92.

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- Garcia, I.; Bermejo, E.; El-Sawaf, A. E.; Castineiras, A.; West, D. X. Structural Studies of Metal Complexes of 2-Pyridineformamide N(4)-methylthiosemicarbazone. *Polyhedron* 2002, 21, 729–737.
- Holzbecher, Z.; Divis, L.; Kral, M.; Sucha, L.; Lacil, F. V. Handbook of Organic Reagents in Inorganic Analysis; John Wiley: New York, 1976.
- Jasinski, J. P.; Bianchani, J. R.; Gueva, J.; El-Sayed, F. A.; El-Asmy, A. A.; West, D. X. Spectral and Structural Studies of the Cu(II) Complexes of 3,4-Hexanedione Bis(3-azacyclothiosemicarbazones. Z. Anorg. Allg. Chem. 2003, 629, 202–206.
- John, R. P.; Sreekanth, A.; Kurup, M. R. P.; Mobin, S. M. Synthesis and Structural Studies of Novel Co(III) Ternary Complexes containing N(4)-Substituted Thiosemicarbazones of 2-hydroxyacetophenone and Heterocyclic Bases. *Polyhedron* 2002, 21, 2515–2521.
- Jouad, E. M.; Larcher, G.; Allain, M.; Riou, A.; Bouet, G. M.; Khan, M. A.; Thanh, X. D. Synthesis, Structure and Biological Activity of Ni(II) Complexes of 5-Methyl-2-Furfural Thiosemicarbazone. J. Inorg. Biochem. 2001a, 86, 565–571.
- Jouad, E. M.; Riou, A.; Allain, M.; Khan, M. A.; Bouet, G. M. Synthesis, Structural and Spectral Studies of 5-methyl-2-Furaldehyde Thiosemicarbazone and its Co, Ni, Cu, and Cd Complexes. *Polyhedron* 2001b, 20, 67–74.
- Jouad, E. M.; Allain, M.; Khan, M. A.; Bouet, G. M. Structural and Spectral Studies of Thiosemicarbazones derived from 3-Furaldehyde and 3-(2-furyl) propan-2-enal. J. Mol. Str. 2002, 604, 205–209.
- Kovala-Demertzi, D.; Domopoulou, A.; Demertzis, M. A.; Valle, G.; Papageorgiou, A. Palladium(II) Complexes of 2-Acetylpyridine N(4)-Methyl, N(4)-Ethyl and N(4)-Phenyl-Thiosemicarbazones. Crystal Structure of Chloro(2-Acetylpyridine N(4)-Methylthiosemicarbazonato) Palladium(II). Synthesis, Spectral Studies and Antitumour Activity. J. Inorg. Biochem. 1997, 68, 147–155.
- Kovala-Demertzi, D.; Yadav, P. N.; Demertzis, M. A.; Coluccia, M. Synthesis, Crystal Structure, Spectral Properties and Cytotoxic Activity of Platinum(II) Complexes of 2-Acetylpyridine and Pyridine-2-Carbaldehyde N(4)-Ethyl-Thiosemicarbazones J. Inorg. Biochem. 2000, 78, 347–354.
- Kovala-Demertzi, D.; Demertzis, M. A.; Miller, J. R.; Papadopoulou, C.; Dodorou, C.; Filousis, G. Platinum(II) Complexes with 2-Acetylpyridine Thiosemicarbazone Synthesis, Crystal Structure, Spectral Properties, Antimicrobial and Antitumor Activity. J. Inorg. Biochem. 2001, 86, 555–563.
- Loabana, T. S.; Sanchez, A.; Casas, J. S.; Carcia-Tasende, M. S.; Sordo, J. Synthesis and NMR Spectroscopy of Dichlorobis

(Acetophenonethiosemicarbazone) Mercury(II) formed from Phenylmercury(II) Chloride and Acetophenonethiosemicarbazone: The First Example of Symmetrisation in Organomercury(II)-Thiosemicarbazone Chemistry. *Inorg. Chim. Acta.* **1998**, 267, 169–172.

- McDonald, A. M. G.; Sirichanya, P. The Determination of Metals in Organic Compounds by Oxygen-Flask Combustion or Wet Combustion. *Microchem. J.* **1969**, *14*, 199–206.
- Quiroga, A. G.; Perez, J. M.; Montero, E. I.; West, D. X.; Alonso, C.; Navarro-Ranninger, C. Synthesis and Charateterization of Pd(II) and Pt(II) Complexes of p-Isopropylbenzaldehyde N-Protected Thiosemicarbazones Cytotoxic Activity Against Ras-Transformed Cells. J. Inorg. Biochem. 1999, 75, 293–301.
- Shakir, M.; Nasman, O. S. M.; Mohamed; Ajax, K.; Varkey, S. P. Self-Condensation of o-Aminobenzoic Acid in the Presence of Metal Ions. *Polyhedron* **1996**, *15*, 2869–2873.
- Shakir, M.; Chishti, H.; Azim, Y.; Chingsubam, P.; Siddiqi, M. Y. Synthesis and Physico-Chemical Studies on 14- and 16-Membered Octaazamacrocyclic Complexes Derived from Hydrazine with Co(II), Ni(II), Cu(II), and Zn(II). Synth. React. Inorg. Met. Org. Chem. 2003, 33, 1569–1583.
- Tarasconi, P.; Capacchi, S.; Pelosi, G.; Cornia, M.; Albertini, R.; Bonati, A.; Dall'Aglio, P. P.; Lunghi, P.; Pinelli, S. Synthesis, Spectroscopic Characterization and Biological Properties of New Aldehydes Thiosemicarbazones. *Bioorg. Med. Chem.* 2000, *8*, 157–162.
- Vogel, A. I. A Text Book of Quantitative Inorganic Analysis, 4th Ed.; Longmans: London, 1978.
- Welcher, F. J. The Analytical Uses of EDTA; Van Norstrand: USA, 1958.
- West, D. X.; Yang, Y.; Klein, T. L.; Goldberg, K. I.; Liberta, A. E.; Martinez, J. V.; Toscano, R. A. Binuclear Cu(II) Complexes of 2-Hydroxyacetophenone <sup>4</sup>N-Substituted Thiosemicarbazones. *Polyhedron* **1995**, *14*, 1681–1693.
- Wu, H.-P.; Janiak, C.; Reheinwald, G.; Lang, H. 5,5'-Dicyano-2,2'-Bipyridine Silver Complexes: Discrete Units or Coordination Polymers through a Chelating and/or Bridging Metal-Ligand Interaction. J. Chem. Soc., Dalton Trans. 1999, 183–190.
- Youssef, N. S. Separation and Characterization of New Transition Metal Complexes of some Chromone Derivatives. Synth. React. Inorg. Met.-Org. Chem. 2000, 30, 225–238.
- Youssef, N. S.; Hegab, K. H.; Eid, A. E. Synthesis and Coordination Properties of New Chromone Thiosemicarbazones Towards Some Transition Metal Ions. *Synth. React. Org. Met.-Org. Chem.* 2003, 33, 1647–1666.