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Syntheses, Characterization and Biological Evolytion of UO_2 (VI), Sn (IV), Zr (IV), Ti (IV) and Th (IV) Complexes of Thiosemi Carbazide Derivative

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Abstract : New series of complexes of UO_2 (VI), Sn (IV), ZrO (IV), Ti (IV)and Th (IV) of ligand 2-[(4- methyl phenyl) amino]acetyl]-N-phenyl hydrazine carbothioamide (H_2L) have been prepared in ethanol and characterized by IR, ^{1}H NMR, elemental analyses, molar conductivity and TGA. The ligand behaves as neutral bidentate or tetradentate, monobasic bidentate, dibasic tetradentate and coordination take place via the carbonyl oxygen atom, the NH groups and the thiol groups. The ligand produces three binuclear complexes. Complexes of 2-[(4- methyl phenyl) amino]acetyl]-N-phenyl hydrazine carbothioamide were screened for anti-bacterial and antifungal properties, the synthesed compound have exhibited potential activity.

Key words: Thiosemicarazide · Complexes · IR · ^{1}H. NMR · TGA and Biological properties

INTRODUCTION

Thiosemicarbazones and thiosemicarbazides have established as an important class of sulfur donor ligands particularly for transition metal ions [1-3] has been shown to be related due to their metal complexing ability. These compounds have a great variety of biological activity such as antitumour, fungicide, bactereocide, anti-inflammatory and antiviral activities [4-8]. Previously examined the chelating behaviour of some NNS donor thiosemicarbazones having pyrazolone ring in several metal complexes with the object of gaining more information about their nature of coordination and related structural and spectral properties [9, 10]. Thiosemicarbazones are known for their capacity to act as polydentate ligands, as well as for their biological activity [11]. Collins *et al.* [12] have reported that the correlation between structure and anti-mycobacterial activity in a series of 2-acetylpyridine thiosemicarbazones. In many cases, by coordination to different transition metal ions that can be found in biological systems, it is possible to obtain complexes that are more efficient as a drugs than the corresponding free ligands. Copper (II) complexes possess a wide range of biological activity and are among the most potent antiviral, antitumor and anti-inflammatory agents. For example, In addition, Agarwal *et al.* [13] reported the synthesis, antibacterial and antifungal properties of Cu (II) complexes of 4-[N-(benzylidene)amino]-, 4-[N-(4-methoxybenzylidene) amino]-, 4-[N-(4-dimethyl aminobenzylidene)amino]- and 4-[N(cinnamalidene)amino] antipyrine thiosemi carbazone. Also described the synthesis, characterization and antimicrobial activity of some complexes of transition metal ions Co (II), Ni(II) and Cu (II) with a series of thiosemicarbazone derivatives 2-hydroxy-8-R-tricyclo [14]. Recently we describe here the preparation, characterization and biological activity of UO_2 (VI), Sn (IV), ZrO (IV), Ti (IV) and Th (IV) complexes of 2-[(4-methyl phenyl) amino]acetyl]-N-phenyl hydrazine carbothioamide.

EXPRIMENTAL

Preparation of ligand

Reagent grade chemicals were used without purification: The ligand 2-[(4- methyl phenyl) amino]acetyl]-N-phenyl hydrazine carbothioamide (H_2L) was prepared by mixing equimolar amounts of the desired hydrazide (0.01mol) in 20 ml of absolute ethanol and the phenyl is othiocyanate (0.01mol) in 10 ml of absolute ethanol [15,16]. The reaction mixture was refleuxed for 3 hrs. The product was recrystalized several times from ethanol.

Preparation of complexes

General procedure: The complexes were prepared by addition of the uranyl (VI) nitrate, acetate, Sn (IV) chloride, Sn (IV) diphenyl chloride,Ti (IV) acetate, Zirconyl (IV) oxychloride and Th (IV) nitrate in EtOH to

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2-[(4- methyl phenyl) amino]acetyl]-N-phenyl hydrazine carbothioamide (H_2L) in EtOH in a 1:1 or 1:2 molar ratio. The reaction solution was stirred magnetically at 60°C for 6 hrs. The resulting solids were filtered off, washed several times with EtOH and dried under vacum over P_4O_{10}.

Elemental analyses (C, H and Cl) were performed by micro analytical unit of the Univerisity of Cairo. IR spectra were performed as KBr discs using a Perkin-Elmer 1430. ^{1}H NMR spectra were recorded in DMSO- d^6 using 300 MHz Varian NMR spectrometer. The molar conductivity measurements were made in DMF solution (10^{-3}M) using a Tacussel conductometer type CD6N. TGA were carried under N_2 atmosphere usig a Schimazu DT-50 thermal analyzer with heating rate 10°C /min.

Biological procedure: The antibacterial activities of thiosemicarbazone, (H_2L) and their metal complexes were studied by the usual cup-plate-agar-diffusion method [17, 18]. The compounds were screened for their antibacterial activity against the following microorganisms: (a) grampositive *streptococcus pyogenes* (*S. pyogenes*), *staphylococcus aureus* and *Basillus subtilis*, (b) gram negative *Escherichia coli*. The cup-plate-agar-diffusion method comprises of the following steps:

- Preparation of media, sterilization and tubing.
- Sterilization of the cleaned glass apparatus.
- Pouring of the seeded medium into sterilized petridishes and cutting of the cups.
- Pouring of the dilute solution of the compounds into the tubs.
- Incubation at a particular temperature.
- Determination of the “zones of inhibition.”

The composition of the test media is the factor, which often exerts the greatest effect upon the drug activity. This is particularly true for thiosemicarbazones, since inhibitors of these compounds appear to be present in the common bacteriological culture medium. Efficient media of known chemical composition are available for many species such as *S. pyogenes* and *E. coli*. In addition to the composition of the test media, its pH is a factor which may directly or indirectly influence the activity of a drug. The pH of the test media taken for *S. pyogenes* and *E. coli* was adjusted in the range 7.6±0.1. The composition of the basal media used in the experiments was (i) sodium chloride = 6.0 gm, (ii) peptone = 10.0gm, (iii) beef extract = 3.0 gm, (iv) yeast extract = 2.0 gm, (v) sucrose = 1.5 gm, (vi) agar-agar = 3.0% and (vii) distilled water = 1.0 litre. And also specific media Brain Heart Infusion (BHI).

Procedure: The measured quantity of the culture of the test organism (0.5 ml) was added heated (nearly 55°C) agar media tubes. The tubes were shaken well and the inoculated media were poured on to the sterilized petridishes and then allowed to set in a refrigerator maintained at 4-8°C. The test solutions of 500 $\mu g\ ml^{-1}$ and 1000 $\mu g\ ml^{-1}$ dilutions of the respective thiosemicarbazones were prepared in a solution of DMF. Five cups of 5 mm diameter were cut in the culture media on the pertidishes. A compound solution of particular dilution (500 $\mu g\ ml^{-1}$ or 1000 $\mu g\ ml^{-1}$) was put in the outer four cups of one of the petridishes and the second solution was put in the four cups of other petridishes. The central cups of all the petridishes were filled with the controlled solution and all the petridishes were allowed to remain in the refrigerator at 10°C for 1hr. to allow diffusion of the solution. The petridishes were then transferred to an incubator at 35°C and kept for nearly 30 hrs. The zones of inhibition formed were measured with calipers. The control of DMF, showed no activity. The activity of the compounds are represented by size of the diameter in mm. The antifungal activity of the compounds was screened by using filter paper disc diffusion method. The tests were carried out by taking 6 mm diameter filter paper discs against the fungi (*A. niger* and *A. flavus*).

RSULTS AND DISSCUSION

^{1}H NMR Spectra

1- Ligand: The ligand 2-[(4- methyl phenyl) amino]acetyl]-N-phenyl hydrazine carbothioamide (H_2L) was confirmed by elemental analysis, infrared (Table 2) and ^{1}H NMR spectroscopy. The^1 H NMR spectrum of H_2L in DMSO -d6 reveals chemical shifts (δ/ppm) at 9.8 for N(4)H, N(2) H, N(1)H at 10.1, 9.6 ppm, a singlet at ca. 3.8ppm and multiplet at 7.6 ppm are attributed to CH_2 and aromatic protons.

II- Complexes: In complexes (1, 4, 6, 8) and 9, show it is structue (NH-2) attached with Ti ion the signal corresponding to (NH (1, 2) appear at the same position as that of free ligand signal. Where as, the signal corresponding to (H(1, 2) in complexes (5, 10 and 12) disappear up on complex formation, while in complexes (3, 6 and 10) new signal appear at 3.3 ppm which attributed coordinated water [19] and also new signal

Table 1: Colors, elemental analysis and molar conductivitiesof 2-[(4- methyl phenyl) amino]acetyl]-N-phenyl hydrazine carbothioamide

				Found (Calc) %			
No.	Compound	Color Yield (%)	M.Wt	C	H	Cl	Λ^{a}_{M}
	H_2L	Pale brown (75)	314.0	61.1(61.2)	5.7(5.7)	-	
1	$UO_2(H_2L)_2(OAc)_2$	Brown (65)	1016.0	42.7(42.5)	4.1(3.9)	-	
2	$[UO_2(HL)_2]$	Red (70)	896.0	43.0(42.9)	4.0(3.8)	-	13
3	$UO_2(HL)(NO_3)(H_2O)$	Brown-red (60)	663.0	29.3(29.0)	2.9(2.6)	-	15
4	$UO_2(H_2L)_3(OH)(NO_3)$	Pale-brown (70)	1291.0	44.3(44.6)	4.4(4.2)	-	18
5	$(Sn)_2(L)(OH)Cl_5(H_2O)_2$	Pale-brown (65)	779.7	24.3(24.6)	2.7(2.9)	23.1(22.8)	22
6	$[Sn(H_2L)_2(C_6H_5)_2Cl(H_2O)].Cl$	Brown (60)	989.6	53.5(53.3)	5.0(4.8)	7.4(7.2)	102
7	$[ZrO(HL)_2]$	Buff (70)	733.0	52.1(52.4)	4.4(4.6)	-	30
8	$[(ZrO)_2H_2LCl_4.4H_2O]$	Brown (65)	742.0	25.6(25.9)	3.7(3.5)	19.4(19.1)	Insoluble
9	$[TiH_2L(OAc)_4]$	Orange (60)	597.8	48.2(48.2)	4.7(4.9)	-	14
10	$[(Ti)_2L(OH)(OAc)_4(H_2O)_2.2H_2O]$	White (70)	749.6	38.5(38.4)	4.9(5.1)	-	20
11	$Th(L)(OH)(NO_3)$	Yellow (65)	624.0	30.6(30.8)	2.4(2.7)	-	15
12	$Th(HL)(OH)(NO_3)_2$	Buff (70)	686.0	28.2(28.0)	2.4(2.8)	-	20

(H_2L, $C_{16}H_{18}N_4OS$) ligand and its metal complexes. a =Ohm^{-1} cm^2 mol^{-1}

Table 2: Infrared spectral bands (cm-1) for -2-[(4- methyl phenyl) amino]acetyl]-N-phenyl hydrazine carbothioamide and its metal complexes

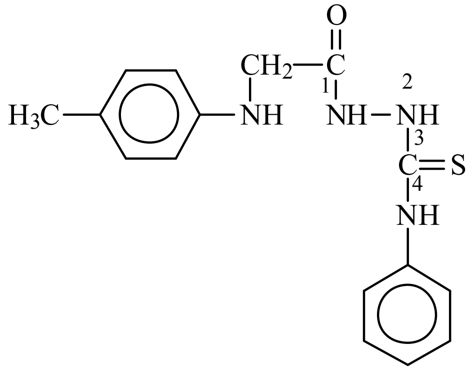
No.	Compound	$\nu(N^4H)$	ν (N^2H)	ν (N^1H)	ν (C=O)	ν (C=S)	ν (M-O)	ν (M-N)	ν (M-S)	ν (M-Cl)
	H_2L	3380(m)	3200(s)	3115(s)	1670(s)	750(s)	-	-	-	-
1	$UO_2(H_2L)_2(OAc)_2$	3320(s)	3250(s)	3100(s)	1645(s)	755(s)	520(m)	430(w)		
2	$UO_2(HL)_2$	3380(m)	3240(s)	3150(s)	-	755(s)	505(w)	470(m)		
3	$UO_2(HL)(NO_3)(H_2O)$	3380(s)	3230(w)	-	-	755(m)	515(m)	435(w)		
4	$UO_2(H_2L)_3(OH)(NO_3)$	3385(s)	3250(w)	3150(s)	1655(s),1625(s)		750(s)	505(s)	445(m)	
5	$(Sn)_2(L)(OH)Cl_5(H_2O)_2$	3385(s)	-	-	-	685(s)	545(s)	495(w)	365(m)	330(s)
6	$[Sn(H_2L)_2(C_6H_5)_2Cl(H_2O)].Cl$	3380(s)	3210(s)	3160(s)	1650(s)	755(s)	540(m)	485(w)		325(m)
7	$[ZrO(HL)_2]$	3270(m)	3220(m)	3130(s)	-	760(s)	535(m)	415(m)	340(m)	
8	$[(ZrO)_2H_2LCl_4.4H_2O]$	3370(w)	3230(s)	3170(s)	1630(s)	755(s)	530(m)	430(w)	350(w)	320(m)
9	$[TiH_2L(OAc)_4]$	3260(m)	3220(s)	3120(s)	1640(s)	755(s)	540(m)	430(m)		
10	$[(Ti)_2L(OH)(OAc)_4(H_2O)_2.2H_2O]$	3370(m)	-	-	-	680(s)	510(m)	440(m)	370(m)	
11	$Th(L)(OH)(NO_3)$	3390(m)	3200(m)	-	-	724(m)	550(m)	470(m)		
12	$Th(HL)(OH)(NO_3)_2$	3350(s)	-	-	1660(s)	685(s)	510(s)	470(m)		

appeared at 12.3-13.0 ppm attributed to singlet OH in complexes (4, 5, 10, 11 and 12).

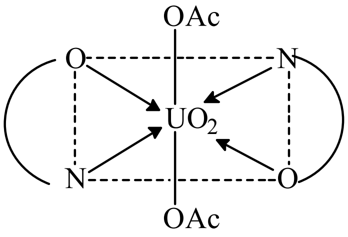
The reaction of the ligand H_2L with different salts of UO_2(VI) acetate, nitrate, $SnCl_4$, $(C_6H_5)_2$ $SnCl_2$, $ZrOCl_2$, Ti(IV) acetate and Th(IV) nitrate gives two types 1:1 and 1:2 metal complexes. These air stable complexes are non-hygroscopic, partially soluble in most organic solvents and in DMF and DMSO freely soluble. The values of molar conductivities in DMF (10^{-3} M) solution (Table 1) show that the complex $[Sn\ (H_2L)_2(C_6H_5)_2Cl\ (H_2O)].Cl$ is 1:1 electrolyte, whereas the other complexes are non-electrolytes [20, 21]. The ligand (H_2L) with the metal salt of tin (IV) chloride and zirconyl oxy chloride and titanium acetate produce binuclear complexes (5, 8 and 10).

Infrared Spectra

1-Ligand: The IR spectrum of the ligand H_2L shows that two strong bands at 1670 and 760 cm^{-1} assigned to ν (C=O) and ν(C=S) respectively. The absence of any bands above 3500 cm^{-1} or in the region 2600-2550 cm^{-1} due to the bands of ν (OH) and ν (SH), respectively, the lack of any signals in the IR spectra of free ligand due to the protons of the -OH or -SH, confirms that the ligand exist mainly in keto- form. Moreover, the absence of two broad bands at 2120 and 1820 cm^{-1} which are due to N-H…O stretching and bending vibration [22], may suggest the absence of intramolecular hydrogen bonding. The three bands at 3380, 3200 and 3115 cm^{-1} in the spectra of the ligand are assigened to ν (N^4-H), (N^2-H) and (N^1-H), while the ν (N-N) [23] vibration is observed at 925 cm^{-1}. Also the bands



H_2L



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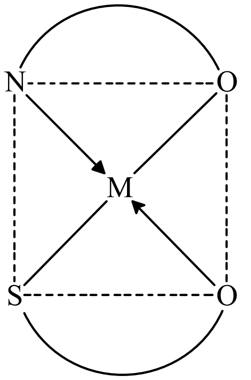

Complex no.

M = UO_2 **(2)**
M = ZrO **(7)**

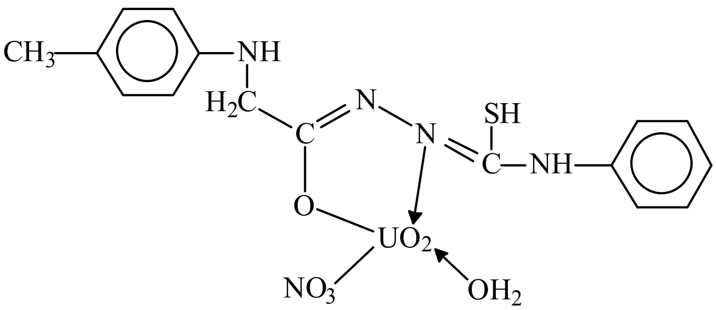

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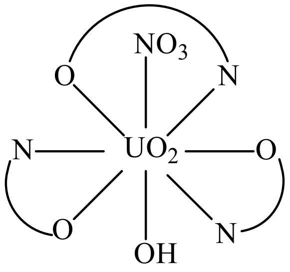
Fig. 1: The suggested chemical structures of ligand and its metal complexes



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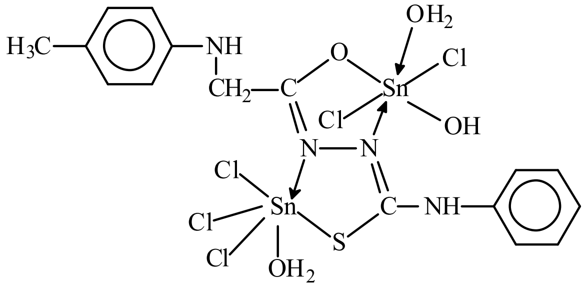

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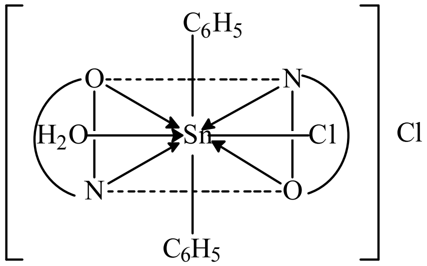

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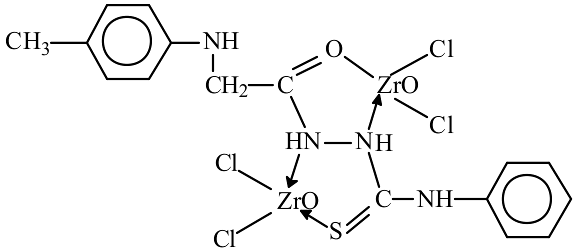

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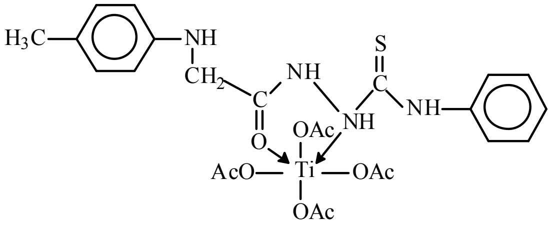

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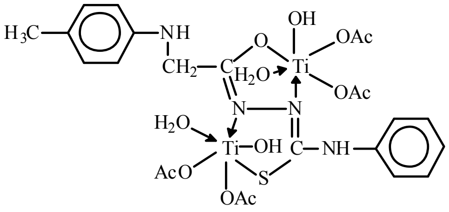

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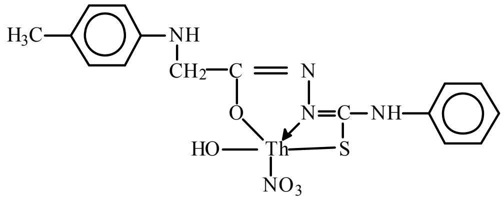

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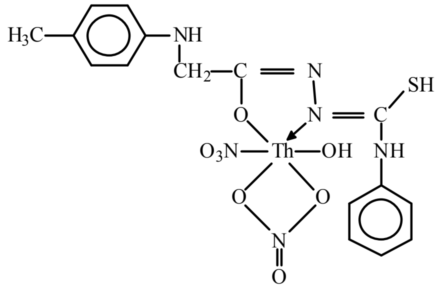

(12)

Fig. 1: Continue

at 1500, 1450 and 1270 cm^{-1} may due to ν(-N-C=S) [24]. These bands are assigned as coupled modes consisting principally of F(NH) and ν(CN).

II-Complexes: Table 2 lists the most important bands that are diagnostic of the mode of coordination of the ligand (H_2L). The infrared spectra of all metal complexes (1, 4, 6, 8) and 9 show a decrease in the energy of ν(C=O) and ν(N-H) compared to these of free ligand upon complexation. The bands appear at 1620-1655, 3210-3250 and 3160 cm^{-1}, respectively, coordination take place via (C=O), (N(2) H) group and in complex (8), the groups of (N(1)H) and (C=S) is added to coordination form and the ligand behave as neutral bidentate and tetradentate in complex(8). While in complexes (2, 3, 7 and 11) the IR spectra show that the ν(C=O) disappear upon complexation, except in complex (12) ν(C=O) shifts to lower frequency, ν(N(1, 2)H) disappear in this complex while the remain complexes ν(N(2)H) shift to lower frequency compared to those ligand and coordination via the enolic oxygen and N(2)H groups, the ligand behave as monobasic bidentate, whereas in complexes(5 and 10), the IR spectra show that the ν(N(1, 2)H), disappear, ν(C=S) shift to lower frequency and ν(C=O) dissappear in complexes upon complex formation and the ligand behave as dibasic tetradentate and coordination take place via thiol sulfur atom, enolic oxygen group, two groups of two (C=N). The IR spectra of all complexes show that the ν(N(4)H) appear at the same frequency or slightly shift, the spectra of the remain complexes show that the ν(C=S) appear at the same frequency compared to those of ligand. The new two bands appear at 1530 and 1590-1600 cm^{-1} and 1530 cm^{-1} assigned to ν (N=N) in complex (12) and ν (C=N) in complexes (2, 3, 5,7, 10 and 11), respectively. The IR spectra of all the complexes reveals new bands at 540-505, 485-410 assigned to ν(M-O) and ν(M-N) [25,26], respectively. The chloro complexes show an additional bands at 325-320 cm^{-1} [27] and in complexes (2, 5, 7 and 10) appear new bands at 370-350 cm^{-1} assigned to ν(M-S) [28]. The IR spectra of UO_2(VI) complexes show a strong absorption band near 905-890 cm^{-1}, assigned to antisymmetric ν_3 (O-U-O)[29]. In monodentate coordination of complexes $UO_2(H_2L)\,(OAc)_{2,}$ $Ti(H_2L)(OAc)_4$ and $(Ti_2)_2L(OH)\,(OAc)_4\,(H_2O)_2$. $2H_2O$ reveal two bands $\nu_a\,(CO_2)$ at 1615-1605 and vs (CO_2) at 1325-1320 cm^{-1} [30], respectively. The IR spectra of complexes (3, 4, 11 and 12) show strong band at 1370-1380 cm^{-1} and 1520 cm^{-1}, weak band at 1285 and 1355 cm^{-1} assigned to $\nu_a\,(NO_3)$ and $\nu_s\,(NO_3)$ respectively, indicating that the NO_3 group coordinates as monodentate and bidentate ligand [31, 32], respectively. The infrared spectra of hydroxo complexes (4, 5, 10, 11 and 12) show bands at 3280-3310 cm^{-1}, assigned to ν(M-OH) [33]. The spectra of complexes (8) and (10) which contain water molecules, show two bands at 3430-3410 cm^{-1} and 1610 (sh), assigned to ν(OH) and δ(H_2O), respectively [34,35]. The above arguments indicat that the ligand behaves as mono basic bidentate, coordination via carbonyl oxygen or enolic oxygen and N (2)H group in complexes (2, 3, 7, 11 and 12), whereas in cmplex(8) the ligand behave as neutral tetradentate and coordination take place via two groups of NH(1, 2), carbonyl oxygen and (C=S). While the ligand in complexes (5 and 10) behave as di basic tetradentate and coordination take place via enolic oxygen atom, thiol sulfur (C-S) and two(C= N) groups.

Thermogravimetric Analysis: Thermogravimetric studies on some solid complexes (6, 3 and 5) indicate that, the complexes $[Sn\,(H_2L)_2(C_6H_5)_2Cl(H_2O)].Cl$, $UO_2(HL)(NO_3)(H_2O)$ and $(Sn)_2\,(L)(OH)\,(H_2O)_2$ exhibit an initial weight loss within the temperature range (180-230°C) corresponding to evolution of one molecule of coordinate water (Found 2.2%, calc.2.0%, Found 2.5%, calc. 2.7% and Found 4.8%, calc. 4.6%). The TGA curves show also that the complexes are thermally stable up to 230°C after this temperature it starts to decompose. The T.G.A. thermograms of complexes (8), (10) $(ZrO)_2(H_2L)\,Cl_4.4\,H_2O$ and $(Ti)_2L(OH)_2(OAc)_4\,(H_2O)_2.2H_2O$ show that these complexes do not show any weight loss up to 260°C, indicating that this complexes are thermally stable up to this temperature. The curves show that the loss of water of hydration or coordinates overlap with the decomposition of the complexes.

Biological properties: A number of authors Padhy΄e and Kauffman [36], Thomas and Parameswaran [37], Murthy and Dharmarajan [38], Taylor *et al.* [39] and Bellaci Ferrari *et al.* [40] investigated the biological and medicinal properties of transition metal complexes of thiosemicarbazones. Thomas and Parmeswaran [37] studied the antitumour activities of Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} chelates of anthracene-9-carboxaldehyde thiosemicarbazone. Murthy and Dharmaraja [38] reported the cytotoxic activity of phenylglyoxal bis (thiosemi carbazone) against *Ehrlich ascites* carcinoma cells. These compounds were also screened for antimicrobial activity on *B. subtilis* and *E. coli*. They inhibited the bacterial growth considerably. Garg *et al.* [41] have recently reported the antifungal activity of some transition metal complexes of 2-(2-hydroxybenzylidene) amino phenyl

Table 3: Antimicrobial activity of 2-[(4- methyl phenyl) amino]acetyl]-N-phenyl hydrazine carbothioamide and its metal complexes

		Antibacterial activity (Zone size in mm)*				Antifungal activity	
No.	Compound	S.p	B.s	*E. coli*	S.a	*A. niger*	*A. flavus*
	H_2L	9	8	9	7	+	+
1	$UO_2(H_2L)_2(OAc)_2$	9	8	9	8	+	+
2	$[UO_2(HL)_2]$	12	12	8	13	+	+
3	$UO_2(HL)(NO_3)(H_2O)$	10	11	8	11	+	+
4	$UO_2(H_2L)_3(OH)(NO_3)$	11	12	10	12	+	+
5	$(Sn)_2(L)(OH)Cl_5(H_2O)_2$	12	11	10	12	+	+
6	$[Sn(H_2L)_2(C_6H_5)_2Cl(H_2O)].Cl$	11	11	9	11	+	+
7	$[ZrO(HL)_{2]}$	10	11	9	10	++	++
8	$[(ZrO)_2H_2LCl_4.4H_2O]$	11	12	11	12	++	++
9	$[TiH_2L(OAc)_{4]}$	12	13	10	11	++	++
10	$[(Ti)_2L(OH)(OAc)_4(H_2O)_2.2H_2O]$	13	12	10	11	++	++
11	$Th(L)(OH)(NO_3)$	12	11	9	12	++	++
12	$Th(HL)(OH)(NO_3)_2$	11	12	10	11	++	++
	Salicylic acid	-	-	-	-	++	++
	Tetracycline	17	15	20	18	-	-
	Ampicillin	20	19	16	21	-	-

benzimidazole. All complexes were screened against *Aspergillus flavus* and *Aspergillus niger* by spore germination inhibition method at concentrations 100, 500 and 1000 ppm using Dithane M-45 as a standard. Recently, Singh [42] have published a review article on metal complexes of glutathione and their biological properties.

In the present studies the antibacterial activities of the Uranyl (VI), Stannic (IV), Zirconium (IV), Titanium (IV) and Thorium (IV) complexes of thiosemicarbazide and standard drugs ampicillin and tetracycline were screened by the agar plate method. In DMF solvent at a concentration of 50 μg ml^{-1} and were tested against Gram positive bacteria *Streptococcus pyogenes*, *Bacillus subtilis* and *staphylococcus aureus* and Gram negative bacteria *Escherichia coli* (Table 3). Diameter of inhibition zone (in mm) of standard drug ampicillin against Gram positive and Gram negative bacteria were found to be (20, 19, 16 and 21) respectively, while tetracycline gave (17, 15, 20 and 18), respectively under the same conditions. Table 3 show that all complexes of thiosemicarbazide have moderate antibacterial activities against these bacteria. Both thiosemicarbazones and used complexes were screened for their antifungal activities against two fungi (*Aspergillus niger* and *Aspergillus flavus)* the results showed that almost all complexes gave nearly the same activities, but they are less active compared to salicylic acid and comparatively faster diffusion of thiosemicarbazide complexes, these compounds were found to be efficient anti fungal and antibacterial agents.

CONCLUSIONS

The structures of the studies complexes are influenced by the nature of the coordinated site of the ligand and by the nature of the metal salt used in their preparation. The ligand behaves as neutral bidentate or tetradentate, monobasic bidentate, dibasic tetradentate and new series of complexes are produced. The studies complexes have moderate anti-bacterial activity against gram positive bacteria (*Streptococcus pyogenes, Bacillus subtilis* and *staphylococcus aureus*) also these complexes have anti-fungal activity against *A. niger* and *A. flavus*, this means that these complexes have medical important.

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