SYNTHESIS AND CHARACTERIZATION OF METAL COMPLEXES OF TRIDENTATE AND HEXDENTATE HYDRAZONE LIGANDS CONTAINING ANTIPYRINE MOIETY

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Abstract:

ZrO(II), Zr(IV), Hf(IV), VO(II), La(III) and Sn(II) complexes of H_2L^1, H_2L^2 and H_2L^3 have been synthesized and characterized by elemental analyses, IR, UV–Vis, conductances, thermal analyses (DTA and TGA). The analyses showed that in all complexes except (5,7, 12, 14) and (19) the ligands behave as monobasic tridentate ligands bonded via the enolic carbonyl oxygen of the hydrazide moiety and coordinated via the azomethine nitrogen and pyrazolone oxygen atoms as in complexes (3-4, 6, 10-11, 13) and (16, 17, 18, 20 and 21) or neutral tridentate ligands coordinated via the ketonic carbonyl oxygen of the hydrazide moiety, the azomethine nitrogen, pyrazolone oxygen atoms as in complexes (2, 9, 15) and (21). In complexes (5, 12 and 19), the ligands behave as monobasic didentate ligands bonded via the enolic carbonyl oxygen of the hydrazide moiety and coordinated via the pyrazolone oxygen atom. In case of complexes (7) and (14), the ligands H_2L^{1-2} behave as dibasic or neutral hexadentate ligands bonded via the carbonyl oxygen of the hydrazide moiety in enolic or ketonic form, the azomethine nitrogen and pyrazolone oxygen atoms.

Keywords: IR spectroscopy, UV-Vis spectroscopy, Antipyrine, Conductivity, Adipohydrazide .

Introduction

Schiff base and hydrazones are widely used in analytical chemistry as selective metal extracting agents as well as in spectroscopic determination of certain transition metals [1]. Hydrazones and their metal complexes have attracted attention due to their wide applications in biological, pharmaceutical, catalysis, spectrophotometric determination, extraction and treatment of wastewater field. They have also photochromisim prosperities [2]. The poly acrolein-isonicotinic acid hydrazone resin is used for the selective separation and preconcentration of palladium and platinum ions in road dust [3]. The dialdehyde cellulose hydrazone derivative was used in treatment of sewage wastewater [4]. 2-hydroxy-1-naphthaldehyde isonicotinoylhydrazone which had iron chelation efficiency and marked as antiproliferative activity and potential for the treatment of cancer [5,6]· Hydrazones also played important roles in improving the antitumor selectivity and toxicity profile of antitumour agents by forming drug carrier systems employing suitable carrier proteins [7].

Investigation of Aim.

Synthesis and study of effect the hydrazone ligands and some metal complexes of on some microorganisms

Expermental

The starting chemicals were of analytical grade and provided from Merck Company (Darmstadt, Germany). IR spectra of the solid ligand and complexes were recorded on Perkin-Elmer infrared spectrometer 681 or Perkin-Elmer 1430 using

KBr disc. The ^{1}H -NMR spectra were recorded with a JEOL EX-270 MHz FT-NMR spectrometer in d_6-DMSO as solvent, where the chemical shifts were determined relative to the solvent peaks. The molar conductivity of the metal complexes in DMSO at 10^{-3} M concentration was measured using a dip cell and a Bibby conductimeter MC1 at room temperature. The resistance measured in ohms and the molar conductivities were calculated according to the equation: $\Lambda=V\times K\times Mw/g\times\Omega$, where: Λ = molar conductivity ($ohm^{-1}\ cm^2\ mol^{-1}$), V = volume of the complex solution, K = cell constant 0.92 cm^{-1}, Mw = molecular weight of the complex, g = weight of the complex, Ω = resistance measured in ohms. Electronic absorption spectra were recorded on a Shimodzu 240 or Perkin Elmer 550 spectrometer using 1-cm quartz cells taking DMSO as solvent. Nujol mull electronic spectra were recorded using whatman filter paper No.1 and referenced against another similar filter paper saturated with paraffin oil. The thermal analyses (DTA and TGA) were carried out in the air on a Shimadzu DT-30 thermal analyzer from 27 to 800 ^{0}C at a heating rate of 10 ^{0}C per minute.Elemental analysis (CHN) was performed in the Analytical Unit within Cairo University (Egypt) by the usual methods of analysis.

Preparation of monohydrazone and dihydrazone ligands

The hydrazone ligands were prepared by standard method [8].

Preparation of metal complexes

All complexes except **(5, 7, 12, 14)** and **(19)** were prepared by adding salts of ZrO(II), Zr(IV), Hf(IV), and La(III) (1 mmol, in 20 mL of ethanol) to hydrazone ligands (1 mmol, in 20 mL of ethanol) in the presence of 1 mmol triethylamine. The mixture was refluxed while stirring for three hours. The resulting solid complexes were filtered off, washed several times with ethanol and dried under vacuum.The complexes **(7)** and **(14)** were prepared by adding salts of Sn(II) (2 mmol, in 20 mL of ethanol) to dihydrazone ligands (1 mmol, in 20 mL of ethanol). The mixture was refluxed while stirring for four hours. The resulting solid complexes were filtered off, washed several times with ethanol and dried under vacuum. The complexes **(5, 12)** and **(19)** were prepared by adding salts of VO(II) (1 mmol, in 10 mL of water) to dihydrazone ligands(2 mmol, in 20 mL of ethanol). The mixture was refluxed while stirring for four hours. The resulting solid complexes were filtered off, washed several times with ethanol and dried under vacuum.

Microbiology:

Fungus Media:

Czapek dox agar medium was prepared by standard method [9]. The chemicals were weighted and redissolved in the DMF (dimethylformamide) as solvent to get the tested concentrations 50 ppm. *Aspergillus Niger* was spread over each dish by using sterile bent Loop rod. Disks were cut by sterilized Cork borer and then taken by sterilized needle. The resulted pits are sites for the tested compounds .The Plates are incubated at 30 ^{0}C for 24- 48 hrs. then any clear zones present were detected.

Bacteria Media:

- Nutrient agar medium was prepared by standard method [9]. The chemicals were weighted and redissolved in the DMF (dimethylformamide) as solvent to get the tested concentrations 50 ppm. *E.coli* was spread over each dish by using sterile bent Loop rod. Disks were cut by sterilized cork borer and then taken by sterilized needle .The resulted pits are sites for the tested compounds. The plates are incubated at 37 ^{0}C for 24- 48 hrs. then any clear zones present were detected.

Results and discussion

The ligands H_2L^1 [N'^{1},N'^{6}-bis((1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)met-hylene)adipohydrazide], H_2L^2 [N'^{1},N'^{4}-bis((1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)methylene)succinohydrazide], H_2L^3 [N'-((1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyr-azol-4-yl)methylene)-2-hydroxybenzohydrazide] and their metal complexes **(2-7),(9-14)** and **(16-21)** were found to be stable at room temperature. The complexes were found to be insoluble in common solvents such as ethanol, acetone, water and chloroform but soluble in DMF and DMSO. The elemental analysis confirmed that the complexes (**2-4, 6, 9, 10, 11, 13, 16, 17, 18, 20** and **21**) were found to be composed form ligands and metal ions with molar ratios equal to 1:1, However, the complexes (5, 12 and 19) were found to be composed form ligand and metal ions with molar ratios equal to 2:1 [Table 1]. On the other hand the complexes **(7)** and **(15)** were found to be composed form ligand and metal ions with molar ratios equal to 1:2. [Table 1].

IR spectra

The infrared spectrum of the ligands showed a strong band in the range 1600-1683 cm^{-1} which assigned to $\nu(C=O^a)$ groups of hydrazide moiety, whereas the two medium bands appeared in the ranges 3240-3328 and 3150-3214 cm^{-1} assigned to the ν(NH) groups [10,11]. These observations indicated that the ligands present in the ketonic form in the solid state [12]. The spectrum of the ligands also showed relatively strong bands in the ranges 1643-1650, 1588-1609 and 958-1025 cm^{-1} which may be assigned to the $\nu(C=O^b)$ of the pyrazolone ring [13,14], ν(C=N) of the azomethine group [15], and the ν(N-N) band [16,17] respectively.The most important signals appeared in the infrared spectra of the metal complexes (**2-7, 9-14** and **16-21**) were presented [Table 2]. By comparison of the infrared spectra of the complexes with that of the free ligands, we can observe the disappearance of the bands characteristic to ν(NH) and $\nu(C=O^a)$ in case of complexes **(7)** and **(16-21)**. This may be due bonding of the ligand to the metal ions in the enolic form via the enolic carbonyl oxygen atom. This result is supported by the appearance of a new bands in the ranges 1595–1605 cm^{-1} and 1575–1583 cm^{-1} which may be assigned to the conjugated system ν(C=N-N=C)and $\nu(N=C–O^a)$ respectively [17,18]. In case of complexes **(2-6, 10-13)** and **(14)** the ligands H_2L^1 and H_2L^2 coordinated to the metal ions via only one arms. These results attiened from the appearance of new bands in the ranges 1644-1679, 1615-1641, 1556-1598 cm^{-1} assinged to the carbonyl oxygen of the hydrazided moiety, carbonyl oxygen of pyrazolone ring and ν(C=N) of the azomethine group respectively. This finding indicates that the carbonyl oxygen of the hydrazided moiety and carbonyl oxygen of pyrazolone atoms take part in the coordination with metal ions [13, 14]. At the same time, the characteristic band of the ν(N–N) which appeared in the spectra of the ligand in the range 958-1025 cm^{-1} shifted to higher frequency and appearing in the range 997–1029 cm^{-1}. The lowering of the ν(C=N) frequency and the higher frequency of the ν(N–N) band confirmed the hypothesis which stated that the azomethine nitrogen atom participated in coordination with the metal ions [19]. The appearance of a new bands appeared in the ranges 539–670 and 447-513 cm^{-1} for different complexes may be assigned to the (M←O) and ν(M←N) respectively [17, 20]. These findings were taken as indication that the ligands were coordinated with the metal via carbonyl oxygen atoms of the hydrazide moiety and pyrazolone and the azomethine nitrogen atoms. The spectra of complexes **(5, 12)** and **(19)** showed a band located in the range 948-979 cm^{-1} which may be assigned to ν(V=O) frequency [13,21]. Complexes **(2, 9)** and **(16)** showed band in the range 736-798 cm^{-1} assigned to the ν(Zr=O) [22] frequency. In all complexes there are a broad bands appeared in the range 3403–3482 cm^{-1} assigned to water molecules [12]. Based on the foregoing discussions together with the results of elemental analysis we can say that in all complexes except **(7)** and **(14)** the ligands behave as monobasic tridentate ligands bonded via the enolic carbonyl oxygen of the hydrazide moiety and coordinated via the azomethine nitrogen and pyrazolone oxygen atoms as in complexes **(3-4, 6, 10-11, 13)** and **(16-21)** or neutral tridentate ligands coordinated via the ketonic carbonyl oxygen of the hydrazide moiety, the azomethine nitrogen, pyrazolone oxygen atoms as in complexes **(2)** and **(9)**. In case of complexes **(7)** and **(14)** the ligands H_2L^{1-2} behave as dibasic or neutral hexadentate ligands bonded via the carbonyl oxygen of the hydrazide moiety in enolic or ketonic form, the azomethine nitrogen and pyrazolone oxygen atoms.

^{1}H-NMR spectra

The ^{1}H-NMR spectrum of the ligands H_2L^{1-3} measured at room temperature using d_6-DMSO showed that the ligand is present in two isomers in their ketonic form [8, 23]. This conclusion was gained from the presence of two peaks for the N-*H* group located 10.85-12.3 ppm [12,13, 24, 25] and azomethine group *H*—C=N which located in the range 7.8-8.35 ppm [11,19]. The integration of the two sets of signals related to N-*H* and *H*—C=N groups clarified that the ratio between the two isomers was in the range 42:58. The spectrum also showed a set of peaks observed as multiple in the range 6.8-7.85 ppm that may be assigned aromatic protons [10, 13, 24, 25]. The signal which appeared in the ranges 3.2-3.3 and 2.50-2.55 ppm may be assigned to (N—CH_3) and (C—CH_3) of the ligand respectively [14, 24, 25]. The signal appeared at 2.49 and 1.64 ppm may be assigned to (CH_2—CH_2) and (CO—CH_2) [26, 27] respectively. Based on the previous finding it is clear that the ligand is present only in the keto form. This finding was confirmed from the appearance of the N*H* signal (11.05 ppm) and absence of the OH signal of the enolic form. Many authors [12, 28] reported the same conlusion.

The molar conductivity

The molar conductivities of 1×10^{-3} M solutions of the metal complexes in DMSO solvent at room temperature were found to be ranged between 5.0 and 33.5 ohm^{-1} cm^2 mol^{-1} [Table 1]. These values refered to the non-electrolytic nature of all complexes. The considerable high conductance values for some complexes may be due to the partial solvoysis of them [29,30].

Electronic absorption spectra of the ligands and there metal complexes

The electronic absorption spectrum of the ligands H_2L^1, H_2L^2 showed that the ligand exhibits three bands in the ranges 255- 260, 300-315 and 315-325 nm. The first one assigned to intraligand $\pi\rightarrow\pi^*$ transition in the benzoniod moiety which nearly unchanged on complexation. The second and third bands may be assigned to the $n\rightarrow\pi^*$ and charge transfer transition of the azomethine and carbonyl groups. These bands shifted to higher energy on complexation indicating the participation of these group in coordination with metal ions [12, 31] The electronic absorption spectrum of the thried ligand H_2L^3 exhibits five bands located at 265, 310, 320, 350 and 380 nm The first one which appeared at 265 nm may be attributed to $\pi\rightarrow\pi^*$ transition of the benzenoid moiety of the ligand, whereas the second one which appeared at 310 nm may be attributed intraligand $\pi\rightarrow\pi^*$ transition. The third band appeared at 320 nm may be attributed to hydrogen bonding. The last two bands which appeared at 350 and 380 nm may be assigned to $n\rightarrow\pi^*$ transition of the azomethine and carbonyl groups. These bands were found to be shifted to lower energy on complexation indicating the participation of these groups in the coordination with metal ions [12, 18]. In addition, the spectra of the complexes were showed new bands observed in the range 340–370 nm, which may be attributed to the charge-transfer bands [31]. Usually electronic absorption spectra of the six coordinate oxovanadium(IV) complexes d^1 are characterizaed by the presence of three absorption bands corresponding to $^2B_2\rightarrow{}^2E$ ($d_{xy}\rightarrow d_{xz}$, d_{yz}), $^2B_2\rightarrow{}^2B_1$ ($d_{xy}\rightarrow d_{x2-y2}$), $^2B_2\rightarrow{}^2A_1$ ($d_{xy}\rightarrow d_{z2}$). The electronic absorption spectra of complexes **(5, 12)** and **(21)** in DMSO solution showed a broad band centered in the range 660-685 nm which may be assigned to superimposed transitions $^2B_2\rightarrow{}^2E$ ($d_{xy}\rightarrow d_{xz}$, d_{yz}), $^2B_2\rightarrow{}^2B_1$ ($d_{xy}\rightarrow d_{x2-y2}$), $^2B_2\rightarrow{}^2A_1$ ($d_{xy}\rightarrow d_{z2}$) [25]. This indicates that the oxovanadium complexes have a distorted octahedral geometry. The electronic absorpation spectra of the zirconyl(II), zirconium(IV) and hafinium(IV)complexes **(2-4)**, **(9-11)** and **(16-18)** in DMSO solution exhibit bands appeared in the ranges 445-565 and 375-400 nm awhich may be assigened to charage transfer and d-d transitions respectively [22,35]. Based on the results of elemental, thermal analyses, IR, ^1H -NMR, mass and electronic spectra, electron spin resonance as well as molar conductivity and magnetic moment measurements the structural formula of the studied complexes was suggested had been diamagnetic complexes.

Thermal Analyses (DTA and TGA)

The results of TGA and DTA analyses of complexes are shown [Table 4]. The results show good agreement with theoretical formula as suggested from the analytical data [Table 1]. Complexes **(2)**, **(3)**, **(20)** and **(21)** lost hydrate water molecules in the temperature 75-100 ^0C range and were accompanied by an endothermic peak. The coordinated water molecules were eliminated from their complexes at relatively higher temperature than those of the hydrate water molecules (Table 4). The removal of an HCl molecule was observed for **(2)**, **(3)**, **(20)** and **(21)** complexes in the temperature 240-310 ^0C range, which was accompanied by an endothermic peak. The complexes decompose through degradation of the hydrazone ligand at a temperature over than 500 ^0C leaving metal oxides (530-550) range. The thermal decomposition of complex **(2)** can be represented as follows:

$$[H_2L^1ZrOCl_2(H_2O)].8H_2O \xrightarrow{70\ ^0C} [(HL)ZrOCl(H_2O)] + 8H_2O$$

$$[H_2L^1ZrOCl_2(H_2O)] \xrightarrow{120\ ^0C} [(HL)NiCl_2] + H_2O$$

$$[\ H_2L^1ZrOCl_2] \xrightarrow{290\ ^0C} [(HL)ZrO] + Cl_2$$

$$[\ H_2L^1ZrO] \xrightarrow{440,\ 540\ ^0C} ZrO_2 + \text{volatile organic residue}$$

The thermal data are shown [Table 4].

Biological activity

The antibacterial and antifungal activities of their ligands and their metal complexes were screened using the disk diffusion method [36, 37]. The variation in the effectiveness of different compound against different organisms either depends on the impermeability of the cell of the microbes or differences in ribosomes of microbial cells [38-40]. The in vitro antimicrobial activity of the synthesized compounds was assayed on bacterial and fungal strains. All the compounds showed a good antibacterial activity against Gram-negative bacteria (*Escherichia coli*). Compund (**15**) proved to be the most effective, against on bacteria. Complex (**4**) was given a high activity against on *Aspergillus Niger*. However, there is a marked increase in the bacterial and fungi activities. The zone effect of this compound showed in Fig. 4.

Conclusion

From the above results, we can conclude with the following remarks:

1. The ligands behave as monobasic tridentate ligands, neutral tridentate ligands, monobasic didentate ligands and the ligands H2L1-2 behave as dibasic or neutral hexadentate ligands.
2. All metal complexes are diamagnetic complexes.
3. The antibacterial and antifungal activities of their ligands and their metal complexes showed that, complex (**15**) proved to be the most effective, against on bacteria and complex (**4**) was given a high activity against on fungi.

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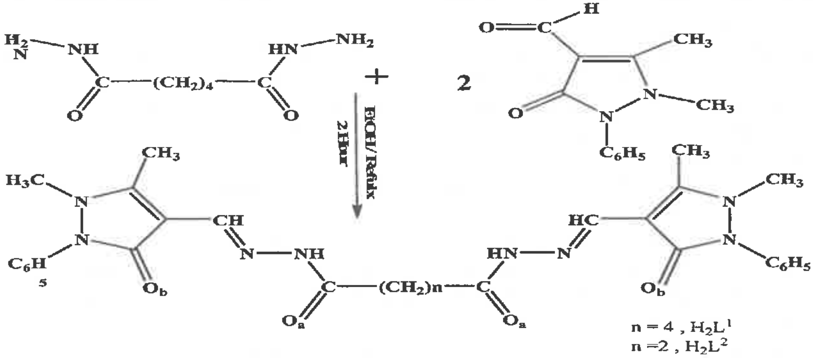


[Fig. 1]

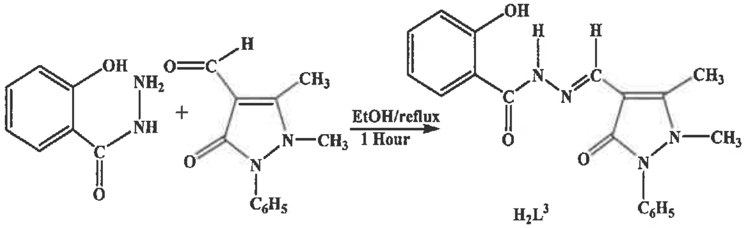


Fig. 2

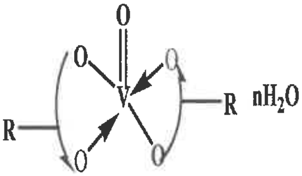
Fig. 1 and 2: Structural of the ligands

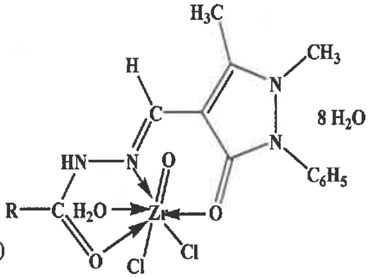
$[VO(HL^{1\text{-}3})_2].nH_2O$

R= $C_{30}H_{33}N_8O_2$, n= 6 (5)

R=$C_{28}H_{29}N_8O_2$, n= 3 (12)

R=$C_{19}H_{17}N_4OH$, n= 2 (19)





$[ZrO(HL^1)Cl_2(H_2O)].8H_2O$

R= $C_{17}H_{21}N_4O_2$, n= 8 (2)

$[M(HL^{1\text{-}3})Cl_3].nH_2O$

R= $C_{17}H_{21}N_4O_2$

M = Zr, n = 3 (3)

M = Hf, n =4 (4)

R=$C_{15}H_{17}N_4O_2$

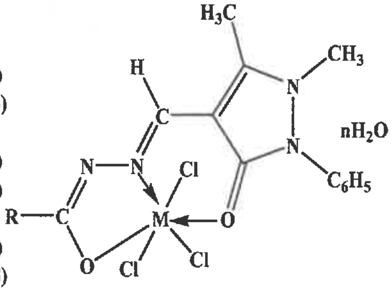
M = Zr, , n= 3 (10)

M = Hf , , n = 4 (11)

R=C_6H_4OH

M = Zr, n = 3 (17)

M = Hf, n =4 (18)

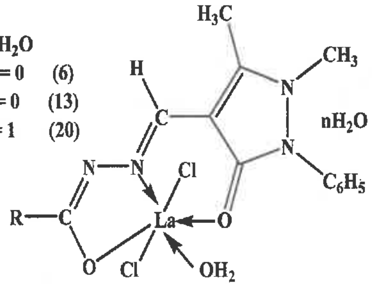


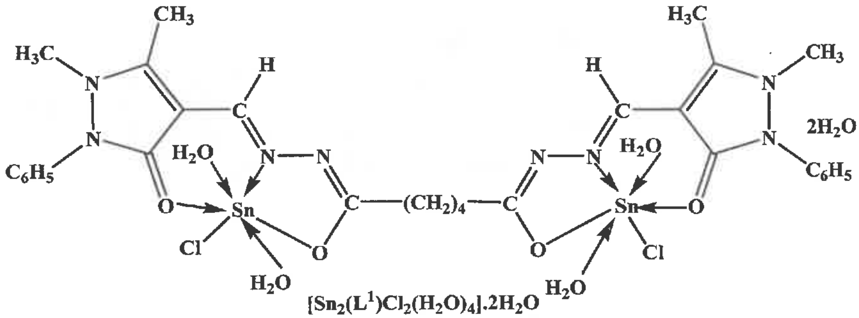
$[La(HL^{1-3})Cl_2(H_2O)].nH_2O$

$R= C_{17}H_{21}N_4O_2$, n= 0 (6)

$R=C_{15}H_{17}N_4O_2$, n= 0 (13)

$R=C_6H_4OH$, n= 1 (20)

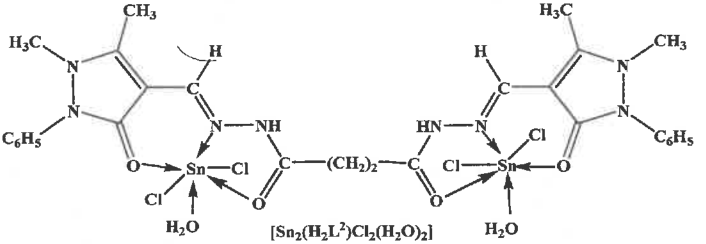




$[Sn_2(L^1)Cl_2(H_2O)_4].2H_2O$

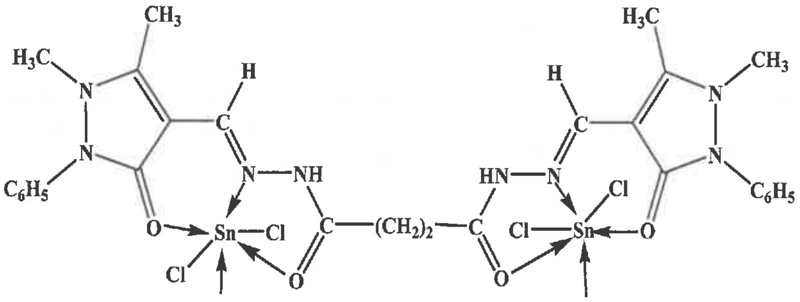
(7)

Fig. 3 Structural representation of the metal complexes

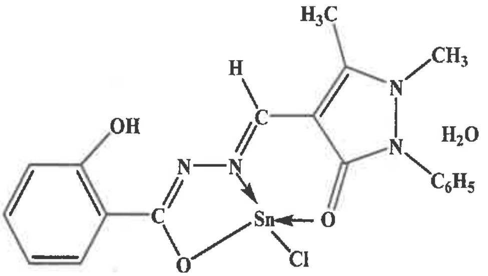


$[Sn_2(H_2L^2)Cl_2(H_2O)_2]$

(14)



$[Sn_2(H_2L^2)Cl_2(H_2O)_2]$
(14)



$[Sn(HL^3)Cl].H_2O$
(21)

Continoued Fig. 3

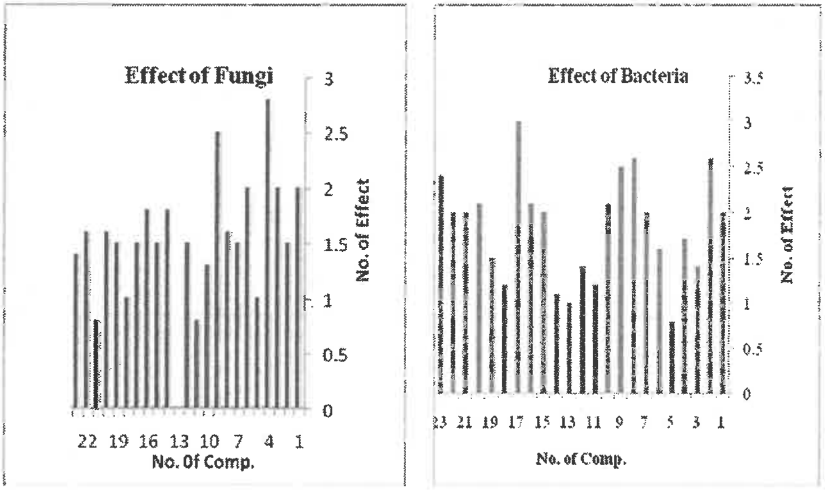


Fig. 4:- The effect of ligands and there metal complexes on microorganisms by used DMF as a standered salution

Table 1. Analytical and some physical Characteristics for the ligands and there metal complexes.

No.	Compound/Complex	Color	B	M. Wt.	Caled (Found) %			Λ^{a}_{M}	Yeild
			(°C)		C	H	N		(%)
1	H_2L^1 ($C_{30}H_{34}N_8O_4$)	White	278	570.6	63.1(62.9)	6.0 (5.8)	19.6 (19.4)	--	85
2	$[H_2L^1(ZrO)Cl_2(H_2O)].8H_2O$	Yellowish white	>300	910.9	39.5 (40.0)	5.7 (5.5)	12.3 (12.4)	13	70
3	$[HL^1(ZrCl_3].4H_2O$	Yellowish white	>300	839.2	42.9 (43.2)	4.9 (5.1)	13.4 (13.5)	5.3	63
4	$[HL^1HfCl_3]$ $4H_2O$	Yellowish white	>300	854.4	54.8 (55.1)	6.1 (6.1)	17.0 (17.1)	8.4	65
5	$[(HL^1)_2VO].6H_2O$	Dark green	>300	1314.3	42.9 (42.4)	5.2 (5.1)	13.3 (13.0)	33.5	70
6	$[HL^1 LaCl_2.H_2O]$	White	>300	797.4	45.1 (45.9)	4.4 (4.1)	14.1 (14.3)	14.1	67
7	$[L^1 Sn_2Cl_2(H_2O)_4].2H_2O$	White	>300	985.1	36.6 (36.4)	4.5 (4.6)	11.4 (11.6)	15.3	73
8	H_2L^2 ($C_{28}H_{30}N_8O_4$)	White	250	542.6	62.0 (61.6)	5.6 (5.5)	20.7 (20.4)	--	85
9	$[HL^2ZrOCl].6H_2O$	Yellowish white	>300	828.4	40.6 (40.5)	5.4 (5.3)	13.5 (13.7)	0.5	69
10	$[HL^2ZrCl_3].3H_2O$	Yellowish white	>300	811.2	41.4 (41.2)	4.6 (4.4)	13.8 (12.5)	21.1	67
11	$[HL^2HfCl_3].4H_2O$	Yellowish white	>300	1206.2	55.7(55.2)	5.5 (5.3)	18.6 (18.3)	13.8	68
12	$[(HL^2)_2VO].3H_2O$	Dark Green	>300	759.6	44.2 (44.0)	4.7 (4.5)	14.7 (14.6)	30.2	75
13	$[HL^2 LaCl_2.H_2O]$	Yellow	>300	787.5	42.7 (42.4)	4.2 (3.9)	14.2 (13.9)	10.5	67
14	$[H_2L^2 Sn_2Cl_4(H_2O)_2]$	White	>300	957.9	35.1 (34.9)	3.4 (3.2)	11.7 (11.9)	11.5	73
15	H_2L^3 ($C_{19}H_{18}N_4O_3$)	Yellowish white	211	350.4	65.1 (65.2)	5.2(5.3)	16.0 (15.7)	--	95
16	$[HL^3ZrOCl(H_2O)_2].2H_2O$	Pale yellow	>300	564.1	40.4 (40.2)	4.4 (4.3)	9.9 (9.8)	23.5	76
17	$[HL^3ZrCl_3].2H_2O$	Pale yellow	>300	583.0	39.1 (38.9)	3.6 (3.5)	9.6 (9. 4)	17.3	60
18	$[HL^3HfCl_3].2H_2O$	Pale yellow	>300	670.3	34.0 (34.0)	3.1 (3.0)	8.4 (8.1)	6.1	61
19	$[(HL^3)_2VO]$. $2H_2O$	Dark green	>300	803.8	56.7 (57.2)	5.0 (4.8)	13.9 (13.9)	27.8	67
20	$[HL^3 LaCl_2(H_2O)].H_2O$	Orange	>300	595.2	38.3 (38.5)	3.5 (3.4)	9.41 (9.12)	9.2	74
21	$[HL^3 SnCl(H_2O)_2]$	White	>300	539.6	42.3 (42.0)	3.9 (3.8)	10.38 (10.16)	11.8	69

[a] Molar conductivity as 10^{-3} M solutions (ohm^{-1} cm^{2} mol^{-1}), B is melting point or decomposition temperature

Table 2. IR spectral assignment for the ligands and there metal complexes.

No.	Compound/Complex	v(latticeH_2O)	v(Coord. H_2O)	NH Cm^{-1}	C=O^a Cm^{-1}	C=O^b Cm^{-1}	C=N Cm^{-1}	N=C-O	N-N Cm^{-1}	M-O	M-N	v(M-Cl)
1	H_2L^1 ($C_{30}H_{34}N_8O_4$)	------	-------	3240,3214	1683	1647	1606	--	958	--	--	------
2	$[H_2L^1(ZrO)Cl_2(H_2O)].8H_2O$	3650-3300	3290-2780	3255,3219	1685,1670	1648,1629	1607,1598	--	1018	670	504	425
3	$[HL^1(ZrCl_3].4H_2O$	3560-3200	--------	3250, 3219	1678	1647,1635	1604,1595	1561	1019	627	479	420
4	$[HL^1HfCl_3]$ $.4H_2O$	3550-3280	------	3250,3220	1679	1649,1631	1604,1598	1563	1016	627	479	418
5	$[(HL^1)_2VO].6H_2O$	3580-3400	-------- 800	3206	1644	1609	1593	1558	1010	536	448	---
6	$[HL^1 LaCl_2.H_2O]$	---------	3300- 2850827	3240	1661	1645,1624	1608,1556	1542	1020	627	504	424
7	$[L^1 Sn_2Cl_2(H_2O)_4].2H_2O$	3600-3270	3100-2900	--	--	1634	1600	1543	1021	638	508	390
8	H_2L^2 ($C_{28}H_{30}N_8O_4$)	....	....	3328,3203	1668	1650	1609	--	958	--	--	-----
9	$[HL^2ZrOCl].6H_2O$	2570-3280	-----	3211	1666	1649,1618	1607,1594	1548	1010	657	513	423
10	$[HL^2ZrCl_3].3H_2O$	3540-3220	----	3195,3101	1664	1645,1615	1606,1578	1548	1012	617	506	423
11	$[HL^2HfCl_3].4H_2O$	3590-3280	------- 820	3201	1665	1649,1641	1610,1593	1546	1012	657	513	421
12	$[(HL^2)_2VO].3H_2O$	3500-2320	----	3180	1665	1647,1625	1606,1586	1554	979	620	497	---
13	$[HL^2 LaCl_2.H_2O]$	--------	3320-2800 828	3250	1666	1649,1631	1605,1595	1546	1012	612	511	419
14	$[H_2L^2 Sn_2Cl_4(H_2O)_2]$	--------	3260-2750	3206	1665	1650,1625	1604,1590	--	991	600	505	423
15	H_2L ($C_{19}H_{18}N_4O_3$)	------	....	3250,3150	1600	1643	1588	--	1025	--	--	-----
16	$[HL^3ZrOCl(H_2O)_2].2H_2O$	3650-3400	3380-3250	--	--	1633	1595,1580	1521	1031	562	480	405
17	$[HL^3ZrCl_3].2H_2O$	3550-3340	------	--	--	1629	1599,1577	1551	1029	539	449	420
18	$[HL^3HfCl_3].2H_2O$	3550-3250	-------	--	--	1640	1599,1575	1541	1025	544	447	416
19	$[(H_2L^3)_2VO].$ $2H_2O$	3570-3360	---- 838	--	--	1617	1601,1583	1535	1027	570	475	---
20	$[HL^3 LaCl_2(H_2O)].H_2O$	3660-3270	3235-2990 755	--	--	1639	1605,1580	1543	1024	565	490	415
21	$[HL^3 SnCl(H_2O)_2]$	-------	3400-3200	--	--	1625	1602,1579	1539	1027	575	465	410

C=O^a is the carbonyl of the hydrazide moiety, C=O^b is the carbonyl of the pyrazolone ring

Table 3. Electronic spectra of the ligands and there metal complexes

No.	Ligand / Complexes	Bands in DMF
1	H_2L^1 ($C_{30}H_{34}N_8O_4$)	325, 315, 255
2	$[H_2L^1(ZrO)Cl_2(H_2O)].8H_2O$	535, 385, 330, 315, 260
3	$[HL^1(ZrCl_3].4H_2O$	465, 390, 330, 310, 260
4	$[HL^1HfCl_3]\ .4H_2O$	450, 375, 330, 310, 260
5	$[(HL^1)_2VO].6H_2O$	685, 390, 360, 345, 310, 255
6	$[HL^1\ LaCl_2.H_2O]$	345, 325, 255
7	$[L^1\ Sn_2Cl_2(H_2O)_4].2H_2O$	335, 315, 255
8	H_2L^2 ($C_{28}H_{30}N_8O_4$)	315, 300, 255
9	$[HL^2ZrOCl].6H_2O$	555, 400, 330, 320, 260
10	$[HL^2ZrCl_3].3H_2O$	455, 390, 325, 305, 260
11	$[HL^2HfCl_3].4H_2O$	475, 385, 330, 310, 260
12	$[(HL^2)_2VO].3H_2O$	675, 390, 375, 360, 345, 310, 255
13	$[HL^2\ LaCl_2.H_2O]$	325, 310, 255
14	$[H_2L^2\ Sn_2Cl_4(H_2O)_2]$	330, 315, 255
15	H_2L ($C_{19}H_{18}N_4O_3$)	370, 350, 320, 305, 260
16	$[HL^3ZrOCl(H_2O)_2].2H_2O$	565, 400, 380, 325, 310, 255
17	$[HL^3ZrCl_3].2H_2O$	475, 395, 370, 335, 310, 260
18	$[HL^3HfCl_3].2H_2O$	445, 400, 380, 330, 3200, 260
19	$[(H_2L^3)_2VO].\ 2H_2O$	680, 390, 360, 345, 350, 255
20	$[HL^3\ LaCl_2(H_2O)].H_2O$	380, 355, 310, 300, 260
21	$[HL^3\ SnCl(H_2O)_2]$	370, 345, 320, 300, 260

Table 4:- Thermal data for the metal complexes

Comp. No.	Temp. (C^0)	DAT (peak)		TGA (Wt. loss %)		Assignment
		Endo	Exo	Calc.	Found	
(2)	70	endo	---	16.0	15.8	Loss of hydrated water (8 H_2O)
	120	endo	----	2.30	2.70	Loss of coordinated water (1 H_2O)
	290	endo	……..	9.70	10.0	Loss of hydrochloride molecules (2)
	440	----	exo			
	540	----	exo	18.2	17.8	Decomposition with the formation of ZrO_2
(3)	80	endo	----	8.58	8.6	Loss of hydrated water (4 H_2O)
	310	endo	----	14.3	14.0	Loss of hydrochloride molecules (3)
	360	endo	-----			
	450	----	exo			
	540	----	exo	18.7	17.9	Decomposition with the formation of ZrO_2
(20)	75	endo	----	3.0	3.2	Loss of hydrated water (1 H_2O)
	285	endo	----	3.1	3.0	Loss of coordinated water (1 H_2O)
	295	endo	----	13.0	13.2	Loss of hydrochloride molecules (2)
	390	----	exo			
	415	----	exo			
	495	----	exo			
	550	----	exo	31.8	31.2	Decomposition with the formation of LaO
(21)	140	endo	---	6.7	6.6	Loss of coordinated water (2 H_2O)
	240	endo	---	7.3	7.5	Loss of hydrochloride molecules (1HCl)
	370	----	exo			
	470	----	exo			
	520	-----	exo			
	530	-----	exo	28.9	28.5	Decomposition with the formation of SnO