Journal of Al-Nahrain University Vol. 9(2), December, 2006, pp.24-38 Science

Preparation , Characterisation and Biological activities of Some Metal Complexes of [N [2 - (4,5-diphenyl-3-thion-1,2,4-triazole)methyl]diphenyl amine]

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Abstract

[A new Mannich base [N[2-4,5-diphenyl -3-thion-1,2,4-triazole)methyl]; diphenyl amine] **(DH)**, have been prepared and characterized by (FT-IR) Spectroscopy and thermal analysis (TG DTG). (DH) has been used as a chelating ligand to prepare a number of metal complexes with V(IV),Co(II),Cu(II), Pd(II),Pt(IV) and Zn(II). The prepared complexes were isolated and characterized by (FT-IR) and (UV-Vis) Spectroscopy, flame atomic absorption technique, in addition to magnetic susceptibility, conductivity measurement and thermal analysis (TG-DTG). The study of the nature of the complexes formed in (ethanolic solution) following the mole ratio and continuous variation methods, gave results which were compared successfully with those obtained from solid state studies. The apparent stability constant of the complexes have been studied with the time and their color were stable for more than (4) hours. as well as the molar absorptivities have been calculated.The antibacterial activity for the ligand and their metal complexes were studied against two selected micro-organisms **(E.coli)** and **(Staph. Aureus)**, the minimal inhibitory concentration (MIC) have been also studied to determined the low concentration for inhibitio , two antibiotics (Ampicillin and Amoxicillin) have been chosen to compare their activity with those of the new compounds. Further more the antifungl activity against two micro-organism (Panic. Spp and Asp. flaveus) were studied for the ligand and their metal complexes.

Introduction

Interest in substituted of 1,2,4- triazole derivatives as potential antimicrobial and antiviral agents has continued because this class of compounds demonstrated significant activity against different micro-organisms(1,2). A large number of 1,2,4- triazole derivatives have been prepared and many of them, which contain (-SH) group at (3-position) exhibited activities as bactericides,fungicides,analgesic muscle relaxant,insecticidal and others(3,4). The activity of 1,2,4-triazole **mannich bases** attracted much attention, of special interest is the **2- substituted** aminomethyl -3-thione-4,5-diphenyl-1,2,4- triazole which possess central nervous system depressant activity(5).In previous work(6-8) the synthesis and characterization of mannich base derived from (4,5-diphenyl-3-thion-1,2,4-triazole) and (dibutyl or dipropyl or diisobutyl amine) respectively , were found that a synergic effect in the bio - activity took place upon complexation of these ligands with a number of transiton metal ions . Different structural behaviour was reported depending on the type of the metal besides the ligand structure.These results promote us to continue our work, and we here synthesis a new ligand derived from the triazole hetreocyclic ring and diphenyl amine . This was describ an atempt to introduce the aminomethyl moiety in the structure of mercapto triazole ring to investigate the coordination behaviour of the new ligand toward some transition metal ions (V(IV), Co (II), Cu (II), Pd(II), Pt (IV) and Zn (II)) , and to compare the biological activity of the ligand and their complexes with the main ring structure.

Experimental

All chemicals were of highest purity and were used as received.

A-preparation of the Mannich base (DH)

(DH) was prepared as described in our previous work(6-8) ,starting from ethyl benzoate to prepare the **(3 - mercapto - 4 , 5-diphenyl- 1,2,4-triazole)** which was thene reacted with diphenylamine in the presenceof formaline to get the final product;i.e, **(DH)** .

B-Preparation of the metal complexes (1-6)

Ethanonolic solution of each of the following metal ion salts (0.52 mmol) [$VOSO_4.XH_2O$,$CoCl_2.6H_2O$,$CuCl_2.2H_2O$,$PdCl_2(PhCN)_2$,$H_2PtCl_6.6H_2O$ and $ZnCl_2.2H_2O$,] was added to an ethanolic solution (1.15 mmol) of **(DH)** with stirring . The mixture was heated under reflux for one hour during this time a precipitate was formed in the case of the complexes (2,3, 4 and 5). While

ISSN:1814-5922

for complexes (1) and (6), the precipitate was formed immediately upon stirring at room temperature. Stirring was continued for one hour to ensure a completion of reaction .The product in each case was filtered off, washed with hot ethanol and recrystallized from dichloromethane.

C-Study of complex formation in solution

Complexes of (DH) with metal ions were studied in solution using ethanol as a solvent, in order to determined [M: (DH)] ratio in the complex following Molar ratio and Continues variation methods(9,10). A series of solutions were prepared having a constant concentration [10^{-3}M] of the metal ion and (DH). Absorbencies were measured against blanks prepared separately for each concentration of chelating agent at the wavelength of the maximum absorption of the formed complex. The results of complexes formation in solution were listed in Table (1). Fig. (2) show the change in optical density of the observed light with the ratio of L/M^{n+} at λ_{max} for each complex.

D- Stability constant of mannich bases complex

The conditional or apparent(11) stability constant of the **(1:1)** or **(1:2)** [Metal: Ligand] complex were evaluated as fallows:

Two sets of solutions were prepared, the first set of solutions were formulated to contain stoichiometric amount (1ml) of (10^{-3}M) ligand to (1 ml) of (10^{-3}M) of metal ion by placing in to a three series of 10ml volumetric flasks. The solutions of the coloured complexes were diluted to the mark with ethanol. The second set were formulated to contain five fold excess (5 ml) of (10^{-3}M) Ligand, by placing in to a three series of (10ml) volumetric flasks followed by addition of (1ml) of (10^{-3}M) of metal ion solution, the volumes were then completed to the mark with ethanol. The absorbance (**As** and **Am**) of the solutions, were measured at **λmax** of maximum absorption . The stability constant **(K)** ,and the molar absorptivity **(εmax)** have been calculated , were listed in **Table** (5).

E- Study biological activity for mannich base and its complex

The biological activity of the prepared mannich base and their respective complexes were studied against selected types of bacteria which include **Escherichia coli** as (Gram-negative) and **Staphylococcus** aureus as (Gram positive) were cultivated in Nutrient agar medium.

Two **in vitro** techniques were proceeded for studying antibacterial activity against the two strains, DMSO was used as a solvent and as a control, for both techniques, the constructions of the compounds in this solvent were 10^{-3}M.

The first technique was the Disc Sensitivity Test, this method involves the exposure of the zone of inhibition toward the diffusion of micro-organism on agar plate. The plates were incubated for 24hr. at 37 °C, the zone of inhibition of bacterial growth around the disc was observed.

The second technique was to get the sensitivity of each micro - organism toward the new compounds by determining the minimal inhibitory concentration (MIC) which was a chieved by using Tube Dilution Method . The (MIC) of the new compounds for each micro-organism was measured at the lowest concentration of the compound required to inhibit the growth of this micro-organism, these tubes containing different concentrations of the new compounds were incubated at 37 °C for 45 hr.

Furthermore, two of known antibiotics (**Ampicillin** and **Amoxicillin**), were taken as standard to compare their activity with those of the new ligand and their metal complexes ,these antibiotics cover a wide range of structural pharmacological moieties.

In order to complete this study, the new ligand and their metal complexes were tested for their **in vitro** growth inhibitory activity against a pathogenic fungi, i.e. **Aspergillus flavus** and **Penicillum Spp.** on Potato dextrose agar medium and incubated at 30 °C for 72 hr., DMSO was used as a solvent and as a control, for both techniques, the concetration of the compounds in this solvent were 10^{-3}M. The inhibition of fugal growth, expressed in percentage terms, were determined on the growth in test plates compared to the respective control plates, as given by the Vincent equation, **Table** (6).

$$\text{Inhibition \%} = 100\,(C - T) / C$$

Where:

C = Diameter of fungal growth on the control plate.

T = Diameter of fungal growth on the test plate.

Physical measurements and analysis

Melting points were recorded on GallenKamp melting point apparatus and were uncorrected. FT-IR spectra were recorded using FT-IR.8300 Shimadzu in the range of (4000-200) cm^{-1}. Samples were measured as (CsI disc). Electronic spectra were obtained using UV-1650 PC Shimadzu Spectrophotometer at room temperature. The measurements were recorded using a concentration of 10^{-3}M of the complex in dichloromethane as a solvent. The metal content was estimated Spectrophotometrically using Atomic absorption Shimadzu AA670 Spectrophotometer . Conductivity measurements were obtained using Corning conductivity meter 220.These measurements were obtained in DMF as10^{-3}M concentration at 25C°. Magnetic susceptibility measurements were obtained at 25C° on the solid state applying Faraday's method using Bruker BM6 instrument . Thermal analyses were performed using TG-DTG A6200-Thermo Haake.

Results and Discussion

(A)- Elemental Analysis

The physical analytical data of (DH) and its metal complexes are given in Table (1), which are in a satisfactory agreement with the calculated values. The suggested molecular formulas also supported by subsequent spectral and molar ratio, as well as magnetic moment and thermal analysis.

Table (1)
Physical data for (DH) and its metal complexes

Comp. No.	Color	Melting Point a* C°	Yield %	Metal analysis		M:L Ratio *b	Suggested Formula for Isolated precipitate
				Found %	Calc. %		
(DH)	White	149-146	92	-	-	-	$C_{21}H_{22}N_4S$
[1]	Greenish-Blue	180	82	7.61	8.29	1:1	$[VO(DH)SO_4].2CH_2Cl_2$
[2]	Blue	164	90	9.02	8.98	1:1	$[Cu(DH)Cl_2].2C_2H_5OH$
[3]	Green	183	87	8.93	9.72	1:1	$[Cu(DH)Cl_2].CH_2Cl_2$
[4]	Brown	190	75	16.11	15.28	1:1	$[Pd(DH)Cl_2].CH_2Cl_2$
[5]	Red	198	80	15.95	16.22	1:2	$[Pt(DH)_2Cl_2]Cl_2.H_2O$
[6]	White	168	96	11.39	10.61	1:1	$[Zn(DH)Cl_2].C_2H_5OH$

= All complexes were decomposed. (a*)
= Measured in EtOH solvent. (b*)

(B) -Infrared Spectra

The characteristic stretching vibrational modes concerning (DH) and metal their complexes are described in Table (2). (DH) exhibited a strong high intensity bands appeared at (885), (1069, 1096) and (2880, 2968) cm^{-1},and were assigned to the stretching mode of [**ν C=S , ν N-C=S and ν CH$_2$N]** respectively. In the all complexes **(1 - 6)** theligand behave as a bidentate coordinating to the metal throw the sulfur of **thio carbonyl** and **nitrogen of the methylene** group, therefore the bands due to (**ν C=S, ν N-C=S** and **ν CH$_2$N)** were shifted to lower frequency by **(13-20)** , **(5 -9 ,8 -16)** and **(19-27, 26-33)** cm^{-1} respectively ,Table(2).

These observation were further indicated by the appearance of **(ν M-S, ν M-N and ν M-X)** respectively(12) ,Table (2) . As well as a strong band was observed at **(979)** cm^{-1}due to ν V=O stretching mode in complex **[1]** (13) .The band related to sulfate anion in complex **[1]** was observed at (**1508**) cm^{-1} ,which indictes a bidentate behavior of this group (13,14) . A broad band was observed around **(3450 - 3510)** cm^{-1} in the spectra of **[2 , 5 and 6]** complexes , assigned to a **ν O-H** and suggested the presence of a water or ethanol molecules in the complexes (13,14) .

Table (2)

Characteristic Stretching Vibrational Frequencies (cm^{-1}) located in the FT-IR of (DH) and their Metal Complexes

Comp. No.	νC=S	νN-C=S	νCH$_2$-N	νM-S	νM-N	νM-Cl	νM-O	νO-H
(DH)	885 (S)	1069(S) 1096(S)	2877(S) 2966(S)	-	-	-	-	-
[1]	872(m)	1062(m) 1080(m)	2852(m) 2936(m)	475(w)	522(m)	-	589(S)	-
[2]	870(m)	1060(m) 1082(m)	2858(m) 2933(m)	462(w)	528(m)	400(w)	-	3450(b)
[3]	870(m)	1062(m) 1088(m)	2855(m) 2940(m)	447(w)	513(m)	403(w)	-	-
[4]	867(m)	1064(m) 1084(m)	2858(m) 2933(m)	455(w)	530(m)	399(w)	-	3510(b)
[5]	865(m)	1060(m) 1086(m)	2855(m) 2936(m)	462(w)	525(m)	380(w)	-	3452(b)
[6]	870(m)	1064(m) 1088(m)	2850(m) 2940(m m)	455(w)	503(m)	378(w)	-	3466(b)

(C)- Electronic Spectra, Conductance and Magnetic moment studies

The electronic spectra of the metal complexes were recorded for their solution in dichloromethane as a solvent in the range **(200-1100)** nm, Fig.(1).

The greenish-blue spectrum of Vanadyl (IV) **[1]** complex show two main absorption bands, Table (3), which are assigned to the two transition $^2B_2 \longrightarrow {}^2Eg$ and $^2B_2 \longrightarrow {}^2B_1$ respectively in a **square pyramidal** geometry (15,16). The magnetic moment **(2.0B.M)** is higher than spin value of the vanadium metal only, this result indicates a higher orbital contribution (15,17,18) . Conductivity measurement in **DMF** showed that the complex was nonionic, Table(3) .

For complexe **[2]** the measured magnetic moment was **(4.61B.M)** this show the cobalt ion in it's blue complex to be paramagnetic with **(d^7)** configuration in a distorted tetrahedral environment(17,18).

The electronic spectrum of complex**[2]** shows three bands at (18002,15100 and 14220) cm^{-1}, these bands have been assigned to the transition $^4A_2 \longrightarrow {}^4T_{1(P)}$ (19). Assuming **(Td)** symmetry around **Co (II)** ion. The values of racah parameters **(Dq, B', β, and ν$_2$)** have been calculated to be **(374.4)** , **(754.13)** , **(0.67)** and **(6770)** respectively . The value of β **(0.67)** signifies a fair amount of covalent character in metal to nitrogen and sulphur bonds (20-23) .While the value of **(Dq)** to be (374.4) cm^{-1},one should expect a band due the transition $^4A_2$ $^4T_{2(F)}$ in the infrared region at **(3744)** cm^{-1}, which could not be observed in the spectrum of the **Co(II)** complex(24) .As well as if the complex is regulare or distortion can be known value of spin-orbit coupling constant(λ')has been calculated to be **(-174.02)** cm^{-1} ,this constant has been calculated using the following equation:-

$$\mu o.b = \mu s.o - 15.49\ \lambda' / 10Dq$$

Where: **μo.b** =The observed effective magnetic moment .

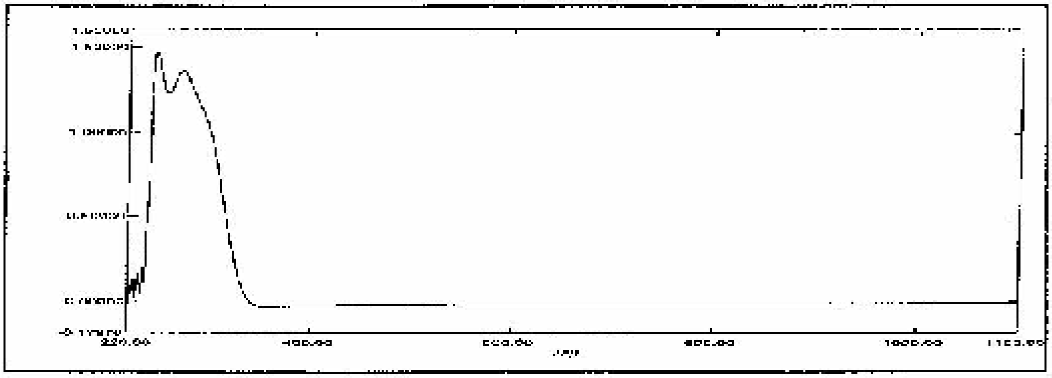
μs.o =The electronic spin only magnetic moment.

The solution spectrum of the dark green complex **[3]** , exhibits intense bands at (11055, 14725, 19908 and 22747) cm^{-1}. The position of these band is in agreement with that reported for a highly distorted octahedral geometry(25,29) .The effective magnetic moment at room temperature was found to be (2.08B.M), which agree well with **square planar** geometry around **Cu(II)** complex (46,47),conductivity measurement showed that the complex was non ionic,Table(3)

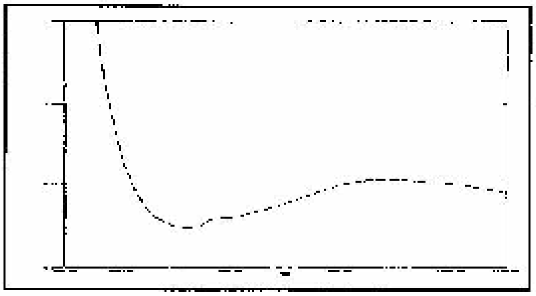
The brown palladium complex **[4]** show three absorption bands which were observed at (22312 , 24941 and 29495)cm^{-1}. The spectrum was a typical of **square planer Pd(II)** complexes (21,28-30). The measured magnetic moment (0.98B.M) showed that the complex to be low spin.

The prepared red Pt (IV) complex **[5]** showed three bands at (19760 , 25982 and 27762) cm^{-1} , which indicate an **octahedral** geometry (9,21,26,28,31). Magnetic moment of solid complex, Table (3), showed a higher orbital contribution (15,32-34) .Conductivity in **DMF** showed that the complex was to be electrolyt, **Table** (3).

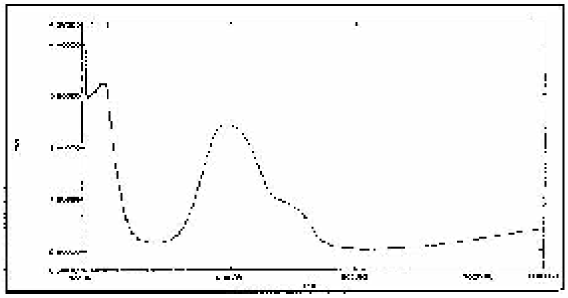
The complex of Zinc (II) wascolorless and was diamagnetic as expected for(**d^{10}**) ion. Since the UV-Vis spectra of the band position was compared with that of the ligand **(DH)** only. The conductivity measurements indicate a non-conducting behavior, Table (3). Thus from the data obtained from FT-IR spectrum, flame atomic absorption and thermal analyses studies, a tetrahedral(34) geometry around Zn(II) ion.



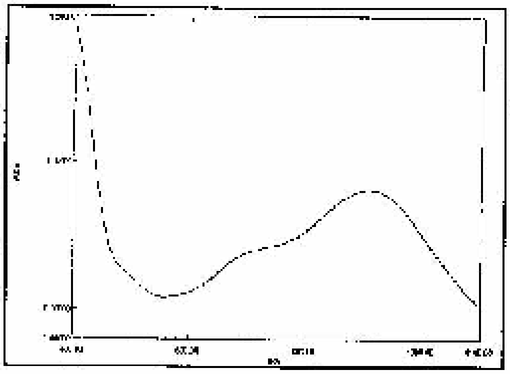
[C$_{27}$H$_{22}$N$_4$S] (DH)



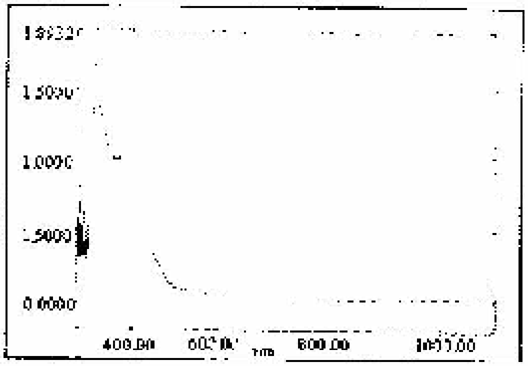
[VO (DH) SO$_4$].2 CH$_2$Cl$_2$ (1)



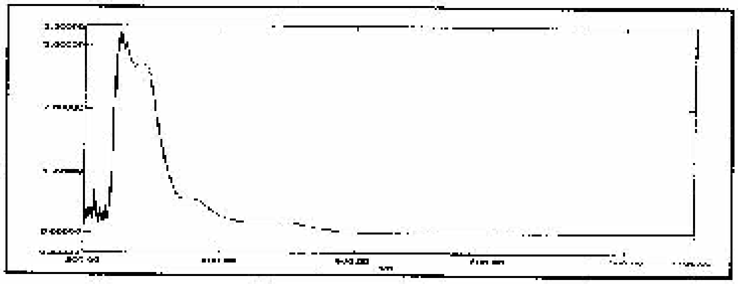
[Co (DH) Cl$_2$].2C$_2$H$_5$OH (2)



Cu (DH)Cl_2].CH_2Cl_2 (3)



[Pd (DH)Cl_2]. CH_2 Cl_2 (4)



[Pt $(DH)_2$ Cl_2]Cl_2. H_2O (5)

Fig.(1)UV-Vis.-Spectra of (DH) and it,s metal complexes

Table (3)

Electronic Spectra (CH_2Cl_2), Conductance (in DMF), and Magnetic moment (B.M) for Metal Complexes

Comp. No.	Bands cm^{-1}	Assignment	10Dq cm^{-1}	Molar cond. $\mu S.cm^{-1}$	μ eff. B.M	Suggested Structure
[1]	11730 17211	$^2B_2g \rightarrow {}^2Eg$ $^2B_2g \rightarrow {}^2A_1g$	-	22.1	2.00	Square pyramidal
[2]	37440 6770 (cal) 15774(av.)	$^4A_2 \rightarrow {}^4T_{2(F)}$ $^4A_2 \rightarrow {}^4T_{1(F)}$ $^4A_2 \rightarrow {}^4T_{1(P)}$	3744	10.9	4.61	Tetrahedral
[3]	11055 14725 19908 22747	$^2B_1g \rightarrow {}^2Eg$ $^2B_1g \rightarrow {}^2B_2g$ $^2B_1g \rightarrow {}^2A_1g$ $L \rightarrow Cu(C.T)$	11055	18.2	2.08	Square planar
[4]	22312 24941 29495	$^1A_1g \rightarrow {}^1B_1g$ $^1A_1g \rightarrow {}^1Eg$ $L \rightarrow Pd(C.T)$	22312	28.7	0.98	Square planar
[5]	19760 25982 27762	$^1A_1g \rightarrow {}^1T_1g$ $^1A_1g \rightarrow {}^1T_2g$ $L \rightarrow Pt(C.T)$	-	168	2.26	Octahedral
[6]	-	-	-	25.05	Dia. Mag.	Tetrahedral

(D)-Thermal analysis

The results for thermogravimetric analysis of (DH) and all complexes (1-6) are given in Table (4). The thermograms have been carried out in the range 25-900 C° at a heating rate of 20 C°/min in nitrogen atmosphere, they showed the following features.-

1- There was an agreement in weight loss between results obtained from the thermal decomposition and calculated values, which supports the results of elemental analysis and confirms the suggested formulae.

2- The ligand (DH) and all the studied complexes showed a common general behavior, in which the first pyrolysis step was the loss of diphenyl amine moiety followed by the other part of the ligand except donor atoms which were left with the metal atom depending on the type of the metal ion.

3- The thermogram of [1-6] complexes at low temperature started with the loss of solvent molecule in outer crystal lattice, Table (4).

4- The final step of the thermolysis reactions of the complexes were found to give the metal oxide [1] and sulfide[3.4 and 6], which indicates the stability of such residues (18). While [2 and 5] , showed incomplete decomposition within temperature range of the experiment, therefore it was not possible to achieve their final product of the thermoly.

Table (4)
Thermal analysis by (TG- DTG) for (DH) and their Complexes

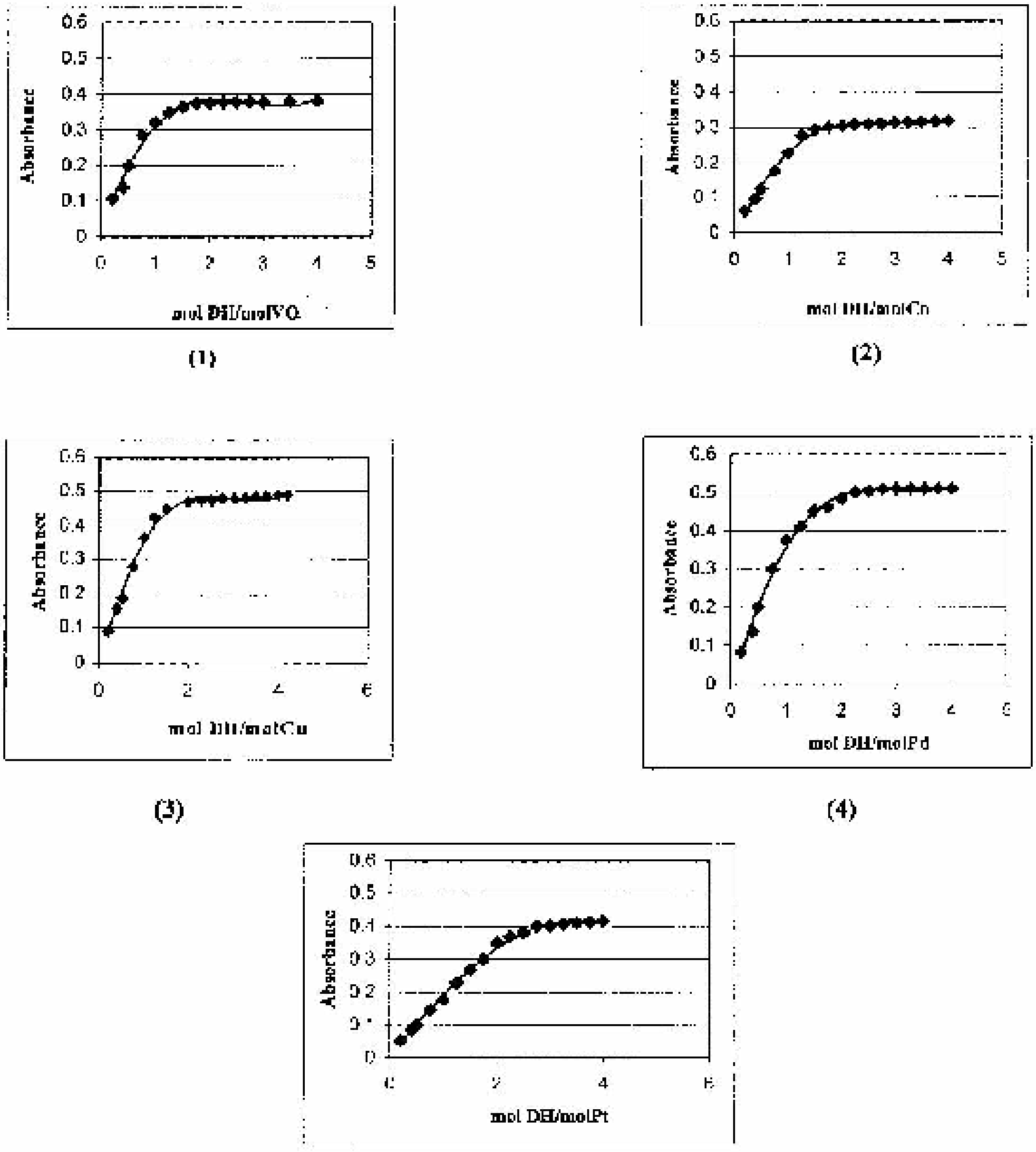
Stable Phase	Temp.range of decomposition C°	%Weight loss Found (Calc.)
(DH) $C_{27}H_{21}N_4S$		
↓ $-2C_6H_5N$	35-278	37.98 (38.71)
↓ $-C_6H_5N$	278-368	20.42(20.94)
↓ $-C_7H_5N$	368-398	24.69 (23.73)
↓ $-CH_2N$	398-422	7.02(6.45)
↓ $-CS$	422-500	9.93 (10.14)
Nothing		
[1] $[C_{27}H_{22}N_4SVOSO_4].2\ CH_2Cl_2$		
$-2CH_2Cl_2$ ↓ $-C_{13}H_{12}N_2$	35-388	48.02 (47.72)
↓ $-C_{12}H_{10}SO_4$	384-478	27.91 (28.43)
↓ $-C_2N_2S_2$	478-525	11.88(10.95)

VO_3	525-900	11.99 (12.90)
[2] $[C_{27}H_{22}SN_4CoCl_2]$. $2C_2H_5OH$		
↓ $-2C_2H_5OH$	35-323	14.11 (14.03)
↓ $-2Cl$ $-C_{26}H_{22}N_4$	323-672	70.02 (70.28)
CuCS	672-900	15.84 (15.69)
[3] $[C_{27}H_{22}SN_4CuCl_2]$. CH_2Cl_2		
↓ $-2Cl$ $-CH_2Cl_2$ $-C_{20}H_{17}N_3$	35-400	68.95 (69.62)
↓ $-C_7H_5N$	400-668	15.36 (15.76)
CuS	668-900	15.22(14.61)
[4] $[C_{27}H_{22}N_4SPdCl_2]$. CH_2Cl_2		
↓ $-CH_2Cl_2$ $-C_{12}H_{10}N$ $-Cl$	35-392	46.60 (46.52)
↓ $-C_{12}H_{10}$	392-448	21.89 (22.11)
↓ $-C_3H_2N_3$	448-625	11.52 (11.49)
PdS	625-900	19.92 (19.87)
[5] $[C_{54}H_{44}N_8S_2PtCl_2]Cl_2$. H_2O		
↓ $-H_2O$ $-4Cl$	35-338	12.80(13.08)
↓ $-C_{24}H_{20}N_2$	338-473	27.11 (27.47)
↓ $-C_{28}H_{24}N_6$	473-559	37.02(36.30)
PtC_2S_2	559-900	23.04(23.15)
[6] $[C_{27}H_{22}N_4SZnCl_2]$. C_2H_5OH		
↓ $-C_2H_5OH$ $-C_{13}H_{10}N$	35-475	34.77(34.72)
ZnS	529-900	15.91(15.80)

Solution study

(1)- Molar ratio and Continuous variation methods

The Molar ratio and Continues variation methods were followed to determine the M:L ratio. The results of complexes in ethanol (solvents), suggest that the metal to ligand ratio was **(1:1)** for **[1,2,3,4,and 6]**, while **(1:2)** for **[5]**, which were comparable to those obtained from solid state study, Table (1).Fig (2).



(1) (2)

(3) (4)

(5)

Fig. (2) Mole ratio plot of (DH)and it,s metal complexes (1-5)

(2)- Stability constant of the mannich base complexes

The apparent stability constant of the (1: 1) [Metal: Ligand] **(eq.1)** or (1: 2) [Metal: Ligand] **(eq.2)** complex ,were evaluated using the following equations(11):

$$K = \frac{(1-\alpha)}{\alpha^2 C} \quad \text{..........................} \quad \textbf{(1)}$$

$$K = \frac{1-\alpha}{4\alpha^3 C^2} \quad \text{..........................} \quad \textbf{(2)}$$

(As and Am) of the solutions, were measured at λmax of maximum absorption,. furthermore the molar absorptivity (εmax) for all complexes were calculated from the **(eq. 3)**(11) :-

(3) A_m = εmax bC

if (α) is the degree of dissociation and **(C)** the concentration of the complex.

The results shown in Table (5), indicate that mole ratio of (1:2) for complex[5], yielded rather high stability constants in contrast to the other values obtained with (1:1) for complexes [1, 2, 3and 4].

Furthermore the molar absorptivity of all complexes is rather high , this probably due to the presence of a bulk aromatic group [diphenyl] on the nitrogen atom of aminomethyl moiety in the structure of 3-thione-4,5-diphenyl -1,2,4- triazole

Table (5)

Stability constant and molar absorptivities of mannich base complexes at room temperature

Complex	**A_s**	**A_m**	**α**	**K L.mol^{-1}**	**εmax L.mol^{-1} cm^{-1}**	**λmax nm**
[1]	0.377	0.439	0.135	6.89 *10^5	3859	756
[2]	0.255	0.299	0.150	3.95 *10^5	3862	563
[3]	0.369	0.441	0.169	5.13 *10^4	4332	668
[4]	0.380	0.459	0.128	6.00 *10^5	4532	415
[5]	0.340	0.397	0.159	5.22*10^{10}	5523	515

Where: -

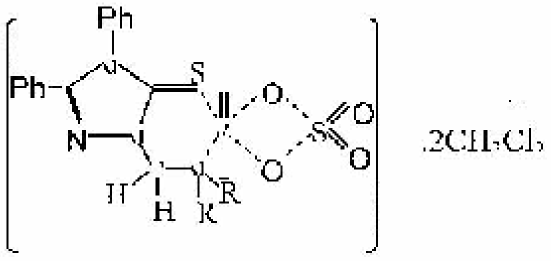
As: Average of three measurements of the absorption of solution containing a stoichiometric amount of ligand and metal ions.

Am: Average of three measurements of the absorption of solution containing the same amount of metal and five fold excess of ligand.

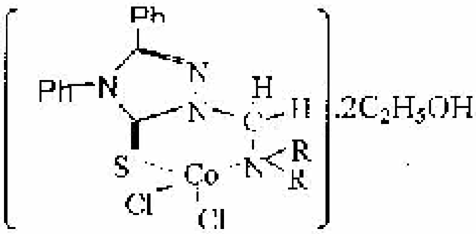
The developed color become stable after one hour, up to four hours.

General Suggested Stereo Chemistry Structure of Complexes (1-6):-

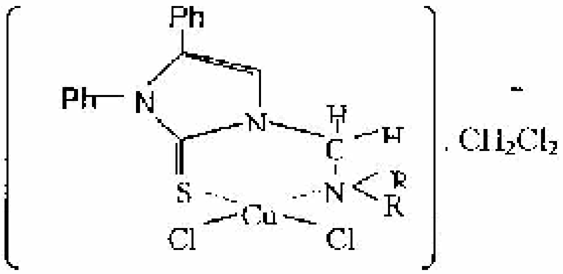
According to the results obtained from the elemental, thermal and spectral analyses the general structure of the above mentioned complexes can be illustrated as follow;-



(1)



(2)



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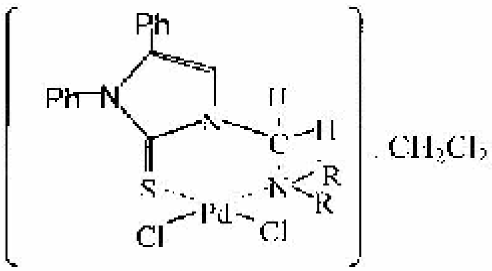
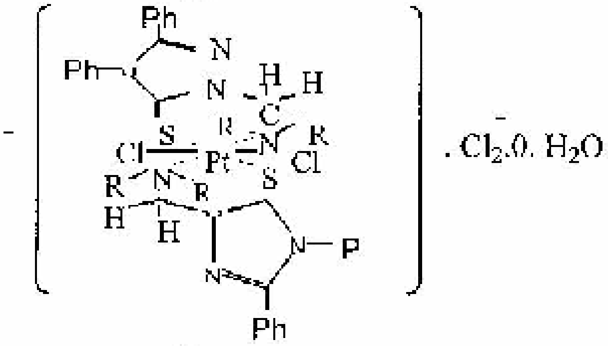
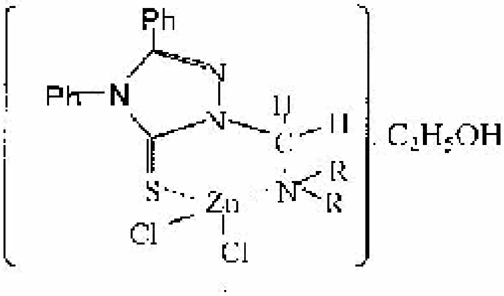


(4)



(5)



(6)

Biological activity

As a result from the above mentioned study, the following points were concluded

a). (DH) was highly active against Staph. Aureus, Table (6).

b). The platinum and palladium complexes showed a wider spectrum of activity against both type of bacteria compared with its ligand.

c). The results reflect the different effects of introducing the metal ion on the ligand structure, where some metal ions enhanced activity, while others retared it, this phenomena is known as Synergistic effect[36]. The difference in synergistic effect between the metal ion and the ligand molecule may be attributed to many factors, of these are V(IV), Co(II), Cu(II) and Zn(II) are considered to be a hard metal ions making their complexes to be less lipophilic, this will relatively retard their pentration through the lipid part of the cell membrane. On the other hand the Pd(II) and Pt(IV) are considered to be soft metal ions, which render their complexes to be more lipophilic, this will facilitate the penetration through the cell wall and affect the constituents of the cell.

d). The results of the (MIC) study for the ligand and their metal complexes are shown in Table (7). These results indicate that some of the new compounds exhibited antibacterial activity against the studied bacteria at lower concentration, while they don't show such activity at higher concentration. As well as (DH ,1 ,2 ,3) and (6) showed high activity at (0.05) μgm.ml^{-1} against E. coli bacteria, while(4) and (5) were active against Staph aureus at (0.025) μ gm.ml^{-1}. On comparison of these values with those of the two antibiotics, it was shown that the new compounds were more active.

e). Study of the antibacterial and antifungal activities revealed that the mannich bases (derived from 3-thione- 4,5-diphenyl-1,2,4-triazole) and their metal complexes, exhibited a greater activity against all the studied micro-organisms compared to that of 3-thione- 4,5-diphenyl-1,2,4-triazole it self[24]. This indicate that introductions of the aminomethyl group on the triazole derivative ring were raise the killing zone.

f). Results of the antifungal activity of the new compounds, Table (6) showed that the metal ion chelates were more toxic compared with their parent ligand toward the same micro-organism and under the identical experimental conditions. The increase in the antifungal activity of metal chelates may be due to the effect of the metal ion on the normal cell process. These activities may be explained by Tweedy's Chelation theory[37], according to which chelation reduces the polarity of the metal atom mainly, because of the partial sharing of its positive charge with the donor groups of the ligand, which favours permeation of the complexes through the lipid layer of cell membrane[38].

Table (6)

Antibacterial and antifungal activities for mannich base and their metal complexes (10^{-3} mgm.ml^{-1})

Compound	E. coli	Staph. aureus	Asp.flavus	Penci. Spp.
Control (DMSO)	-	-	-	-
(DH)	-	10	28	36
[1]	-	15	14	21
[2]	6	8	20	14
[3]	-	15	14	21
[4]	10	10	21	17
[5]	15	25	14	24
[6]	-	-	20	25
	Where: 6-8:(+) 8-10: (++) > 10: (+++)		Where: 30-40: (+++) 20-30 :(++++) 10-20: (+++++)	

Table (7)

Minimal inhibitory concentration (MIC) for mannich base and their metal complexes (μgm. ml^{-1})

Compound	Escherichia coli								Staphylococcus aureus							
	0.025	0.05	0.1	0.25	0.5	1	2.5	5	0.025	0.05	0.1	0.25	0.5	1	2.5	5
(DH)	+	MIC	-	-	-	-	-	-	+	+	+	MIC	-	-	-	-
[1]	+	MIC	-	-	-	-	-	-	+	+	+	MIC	-	-	-	-
[2]	+	MIC	-	-	-	-	-	-	+	+	MIC	-	-	-	-	-
[3]	+	MIC	-	-	-	-	-	-	+	+	+	+	MIC	-	-	-
[4]	+	+	+	MIC	-	-	-	-	MIC	-	-	-	-	-	-	-
[5]	+	+	MIC	-	-	-	-	-	MIC	-	-	-	-	-	-	-
[6]	+	MIC	-	-	-	-	-	-	+	+	+	+	+	+	MIC	-
Ampicillin	+	+	MIC	-	-	-	-	-	+	+	MIC	-	-	-	-	-
Amoxicillin	+	+	+	+	MIC	-	-	-	+	+	MIC	-	-	-	-	-

Where:

(+): Growth

(MIC): 99%

(-): No growth

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الخلاصة

المركبات المحضرة مع نوعين من المضادات (Ampicillin) و (Amoxicillin)، المختارة. كما تمّ إجراء التقويم الحيوي لقاعدة مانخ ومعقداتها المضادة للفطريات على نوعين من الفطريات (-Panic. Spp) و (Asp. flavcus)

تم تحضير قاعدة مانخ الجديدة [4)– 2] N، S – ثنائي فنيل – 3– ثايون 1 ، 2 ، 4– ترايازول) مثيل] ثنائي فنيل أمين [(DH) وشخصت بطرق تحليل طيف الأشعة تحت الحمراء (FT-IR) والتحليل الحراري) TG-DTG (. تم استخدام (DH) كليكاند لتحضير عدد من المعقدات الجديدة مع أيونات عناصر الفناديوم (IV) و الكوبلت (II) و النحاس (II) و البلاديوم (II) و البلاتين (IV) و الخارصين (II). تم عزل المعقدات الجديدة وتشخيصها باستخدام طيف الأشعة تحت الحمراء وطيف الأشعة فوق البنفسجية– المرئية وتقنية الامتصاص الذري اللهبي للعنصر فضلا عن قياسات الحساسية المغناطيسية والتوصيلية الكهربائية والتحليل الحراري (DTG-TG). تمّ كذلك دراسة طبيعة المعقد المتكون في محلول الايثانول باتباع طريقتي النسبة المولية والنسبة المتغيرة

، وقد أعطت هذه الدراسة نتائجاً متطابقة مع تلك التي تمّ الحصول عليها في الحالة الصلبة. كما دُرست ثوابت الاستقرار للمعقدات المتكونة مع الزمن وكانت مدة ثبات اللون أكثر من (4) ساعات.فضلاً عن ذلك تم حساب قيمة الممتصية المولارية للمعقدات. تمّ تقويم الفعالية المضادة للبكتريا لليكاند ومعقداته وأختير نوعين من البكتريا (E.coli) و (Staph. aures) لهذا الغرض ودراسة أقل تركيز يحدث عنده التثبيط (MIC). كما تمّ مقارنة فعالية هذه