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Synthesis, characterization and biological activity of N-phenyl-Ñ-(2-phenolyl)thiourea (PPTH) and its metal complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pd(II), Pt(II) and Hg(II)

BAYAZEED H. ABDULLAH* and YOUSIF M. SALH

Department of Chemistry, College of Science, University of Sulaimani, Sulaimani (Iraq).

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ABSTRACT

A novel thiourea ligand; N-phenyl-Ñ-(2-phenolyl)thiourea (PPTH) is synthesized from the reaction of orthoaminophenol with phenyl isothiocyanate. Treatment of the thiourea ligand PPTH with metal salts $MnCl_2.2H_2O$, $CoCl_2$, $NiCl_2.6H_2O$, $ZnCl_2.2H_2O$ and $CdCl_2.2H_2O$ gave metallic complexes of the types: Tetrahedral $[M(PPTH)Cl_2]$ (M= Mn(II) or Cd(II)), octahedral $[Co(PPTH)_2Cl_2]$, square planar $[Ni(PPT)_2]$ and tetrahedral $[Zn(PPT)_2]$ where the ligand PPTH behaves as a bidentate and coordinated to the metal ion centers through sulfur atom of its thioamide group and either oxygen atom of the hydroxyl group or nitrogen atom of the amine group. Reaction of the ligand PPTH with the metal salts $CuCl_2.2H_2O$, $HgCl_2$, Na_2PdCl_4 and K_2PtCl_4 produced metallic complexes of the types: Tetrahedral $[Hg(PPTH)_2Cl_2]$ and square planar $[M(PPTH)_2Cl_2]$ (M=Pd(II) or Pt(II) or Cu(II)),where, the ligand PPTH behaved as monodentate and coordinated to the metal ion centers through sulfur atom of the thioamide group. All the synthesized ligand metal complexes are characterized by micro-elemental analysis, infrared and ultraviolet-visible spectroscopy, conductivity and magnetic susceptibility measurements. Finally, biological activitiy of the ligand PPTH and its metal complexes are tested against *Escherichia coli* (Gram -ve), *Pseudomonas aeruginosa* (Gram -ve) and *Staphylococcus aureus* (Gram +ve) using well-diffusion method and the results are discussed.

Key words: Thiourea derivative, Transition metal complexes, Biological activity.

INTRODUCTION

Thioureas are important organic compounds: possess high biological activity, act as corrosion inhibitors and antioxidant, and are polymer component[1].Thiourea and urea derivatives show a broad spectrum of biological activities as anti-HIV, antiviral, HDL-elevating, antibacterial and analgesic properties[2-5]. Acyl thiourea derivatives are well known for wide range of biological activities like bactericidal, fungicidal, herbicidal, insecticidal action and regulating activity for plant growth[6-8]. On the other hand, some thiourea derivatives have been used in commercial fungicides[9]. They are selective analytical reagents, especially for the determination of metals in complex interfering materials[10,11]. . Both the ligands and their metal complexes display a wide range of biological activity including antibacterial, antifungal properties[12,13]. Metal complexes of ligands containing sulfur as donor atoms are known to possess antifungal and antibacterial activities[9]. Thiourea and its derivatives coordinate to several transition metal ions to form stable complexes[14] Thiourea are versatile ligands, able to coordinate to metal centres either as neutral ligands, monoanions, or dianions[15]. Oxygen, nitrogen and sulfur donor atoms of thiourea derivatives provide a multitude of bonding possibilities[12,13]. The complexes capacity of thiourea derivatives have been reported in several papers[11,16]. Chelating thiourea ligands containing N, S and O donor atoms show broad biological activity and the existence of metal ions bonded to biologically active compounds may enhance their activities[7].. Thiourea and its

derivatives form a variety of complexes of different symmetries with various metal ions like Ni(II), Pd(II) and Co(II)[18]. N-substituted thioureas form a great variety of complexes with transition metal ions[19].

In this work, N-phenyl-Ñ-(2-phenolyl)thiourea (PPTH) and its metal complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pd(II), Pt(II) and Hg(II) are synthesized , characterized, and their biological activities are measured .

EXPERIMENTAL

Phenylisothiocyanate, ortoaminophenol, potassium chloride, potassium bromide, cesium iodide, $K_2[PtCl_4]$, ethanol and $CdCl_2 \cdot 2H_2O$ were purchased from Fluka AG. Zn(II)chloride, benzene, ether and acetone are Merk products. $PdCl_2$, $CoCl_2 \cdot 6H_2O$, $HgCl_2$, $MnCl_2$, $Pb(CH_3COO)2.4H_2O$, $CuCl_2 \cdot 2H_2O$ and methanol are from supplied by BDH. Ether ,dichloromethane and chloroform are obtained by Alpha. $NiCl_{26}.H_2O$ was purchased from Riedel .

Melting points were measured using Toshinwal Electrothermal Melting point apparatus. Electronic spectra of the ligand and the complexes were measured in DMSO using a Jenway 6485 spectrophotometer. The Infrared spectra of the ligands and complexes were recorded on a SHIMADZU infrared spectrophotometer in the 200-4000 cm-1 range using cesium iodide discs. Elemental analysis was carried out on Perkin Elmer-2400 CHN/O analyzer in Al AL-bayt University IEES/ central Lab. The conductivities of the complexes were measured in DMSO using conductometer type; HANNA instruments, model EC215 Conductivity Meter. Magnetic measurements were recorded on a Bruker BM6 instrument at room temperature following Faraday method **.**

Preparation of the ligand PPTH and its metal complexes

N-phenyl-Ñ-(2-phenolyl) thiourea (PPTH)

Phenylisothiocyanate (2.388cm^3, 0.02mol) was added to a solution of 2-aminophenol (2.18g, 0.02 mol) in ethanol (25 cm^3). The solution mixture was refluxed for three hours to give a white precipitate. Then the solution left to cool in ice-bath to give a white precipitate, which was filtered off, washed with ethanol and diethylether, dried and recrystalized from hot ethanol.

General procedure for preparation of $[Mn(PPTH)Cl_2]$, $[Co(PPTH)_2Cl_2]$, $[Ni(PPTH)_2]$, $[Cu(PPTH)_2Cl_2]$ and $[Zn(PPTH)_2]$

To a solution of PPTH (0.05g, 0.40 mmol) in methanol (5 cm^3) containing a few drops of triethylamine ,a solution of a metal chloride (0.20mmol) in methanol (5 cm^3) was added. The mixture was stirred at room temperature for half to one hour (for $[Zn(PPHT)_2]$ twenty two hours) and a precipitate was formed. Then the solution mixture was cooled in ice-bath for complete precipitation. The product was filtered off, washed with distilled water, methanol and diethylether, and dried under vacuum.

$[Pd(PPTH)_2Cl_2]$

A solution of Na_2PdCl_4 (0.0602g, 0.20mmol) in acetone (5cm^3) was added to a solution of PPTH (0.1g, 0.40mmol) in acetone (3cm^3). The solution mixture volume was reduced to half upon heating in a water-bath and an orange precipitate was formed. Then the solution mixture was cooled in ice-bath and ether was added for complete precipitation. The orange product was filtered off, washed with distilled water and diethylether and dried in vacuum[20].

$[Pt(PPTH)_2Cl_2]$

This complex was prepared as a yellow solid product by a similar method to that used for $[Pd(PPTH)_2Cl_2]$[20].

$[Hg(PPTH)_2Cl_2]$

To a hot solution of PPTH (0.489g, 2mmol) in n-butanol (20cm^3) containing few drops of DMF, a warm solution of $HgCl_2$ (0.543g, 2mmol) in n-butanol (20cm^3) was added. The mixture was digested over a water-bath for thirty minutes, then stirred for another thirty minutes and a white precipitate was formed. The solution mixture was cooled in ice-bath for complete precipitation. The white product was filtered off and washed with cold n-butanol and diethylether and dried in vacuum[21].

$[Cd(PPTH)Cl_2]$

This complex was prepared as a yellow solid product by a similar method to that used for

$[Hg(PPTH)_2Cl_2]$[21].

Biological activity

The biological activity of the ligand PPTH and its metal complexes was measured using well-diffusuion methad[22]. Agar plates were prepared by striking the plates with bacterial inoculum and drying at room temperature. The well of 6-millimeter diameter was cut in the agar plates using a sterilized glass tubes. Finally, 40 µl of solution of each prepared complex (1×10^{-3} M), and the control were added to the labeled wells and the plates were incubated at 37^{0}C for 24 hours. The inhibition zones were measured and the inhibition zone greater than diameter of 6 millimeter were considered as sensitive, while the inhibition zone greatest than diameter of 6 millimeter were considered as highly sensitive, but resistant is refer to unchanged zone .

RESULTS AND DISCUSSION

The ligand N-phenyl-Ñ-(2-phenolyl)thiourea (PPTH) was prepared by reaction of equimolar amounts orthoaminophenol and phenylisothiocyanate in ethanol.It is a white solid, soluble in methanol, hot ethanol, acetone and dichloromethane,but it is insoluble in water and diethylether.

The ligand PPTH was characterized by means of melting point, elemental analysis and infrared spectrum. Elemental analysis data for the synthesized ligand, Table (1), is in consistent with the suggested stoichiometry. The infrared spectrum of the ligand PPTH, showed four characteristic bands at 1543 cm^{-1}, 1452 cm^{-1}, 995 cm^{-1} and 700 cm^{-1}, Table (2), which are attributed to thioamide bands I, II, III, IV respectively[23-25].

The presence of these four bands in the IR spectrum of this ligand indicate the reaction of orthoaminophenol and phenylisothiocyanate and formation of thioamide group in the ligand. The primary (NH_2) group of the reactant orthoaminophenol has two ir bands at 3305 cm^{-1} and 3376 cm^{-1} and upon reaction with phenylisothiocyanate, these two bands are disappeared and a band at 3321 cm^{-1}, Table (2), is appeared which belongs to υ (N-H) of the secondary amine (N-H) of the ligand[26]. This is an indication of the reaction of the orthoaminophenol with phenylisothiocyanate and formation of the ligand (PPTH).

Treatment of the ligand PPTH with metal chloride of (Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II and Hg(II)) in an alcoholic solvent containing few drops of triethylamine gave complexes of the types $[M(PPTH)Cl_2]$, where M=Mn(II) and Cd(II), $[M(PPTH)_2Cl_2]$, where M=Co(II), Cu(II) and Hg(II), and $[M(PPTH)_2]$, where M=Ni(II) and Zn(II). The reaction of the ligand PPTH with metal salts Na_2PdCl_4 and K_2PtCl_4 in acetone gave complexes ; $[Pd(PPTH)_2Cl_2]$ and $[Pt(PPTH)_2Cl_2]$. The prepared metal complexes are characterized as follow:

Elemental analysis data for the synthesized ligand and its metal complexes are shown in Table (1). They are consistent with the suggested stoichiometries. The color and melting points of the synthesized ligand and its metal complexes are also shown in Table (1).

Molar conductivities of all synthesized complexes are measured for (1×10^{-3}M) solution in DMSO at room temperature, Table (1). These measured values are compared with known molar conductivities[27-28] which indicates that they are non-electrolyte and consistent with the proposed formula for them.

The infrared spectra of the prepared ligand and its metal complexes are measured in the range (200-450) cm^{-1} and (400-4000) cm^{-1} using cesium iodide and potassium bromide discs. The characteristic band frequencies are arranged in Table (2). The infrared spectral data were discussed according to the functional groups present in the prepared complexes as follow:

Thioamide bands (HNC=S)

Compounds containing thioamide moiety (HNC=S) usually give rise to four characteristic bands in their infrared spectra. These are: Thioamide band(I) at about 1500 cm^{-1}, band (II) at about 1300-1400 cm^{-1}, band (III) at about 950 cm^{-1} and band (IV) at about 800 cm^{-1}. These bands have contributions from the groups as follows: band (I) has contributions from δ(N-H) + δ(C-H) + υ(C=N), band (II) has contributions from υ(C=S) + υ(C=N)

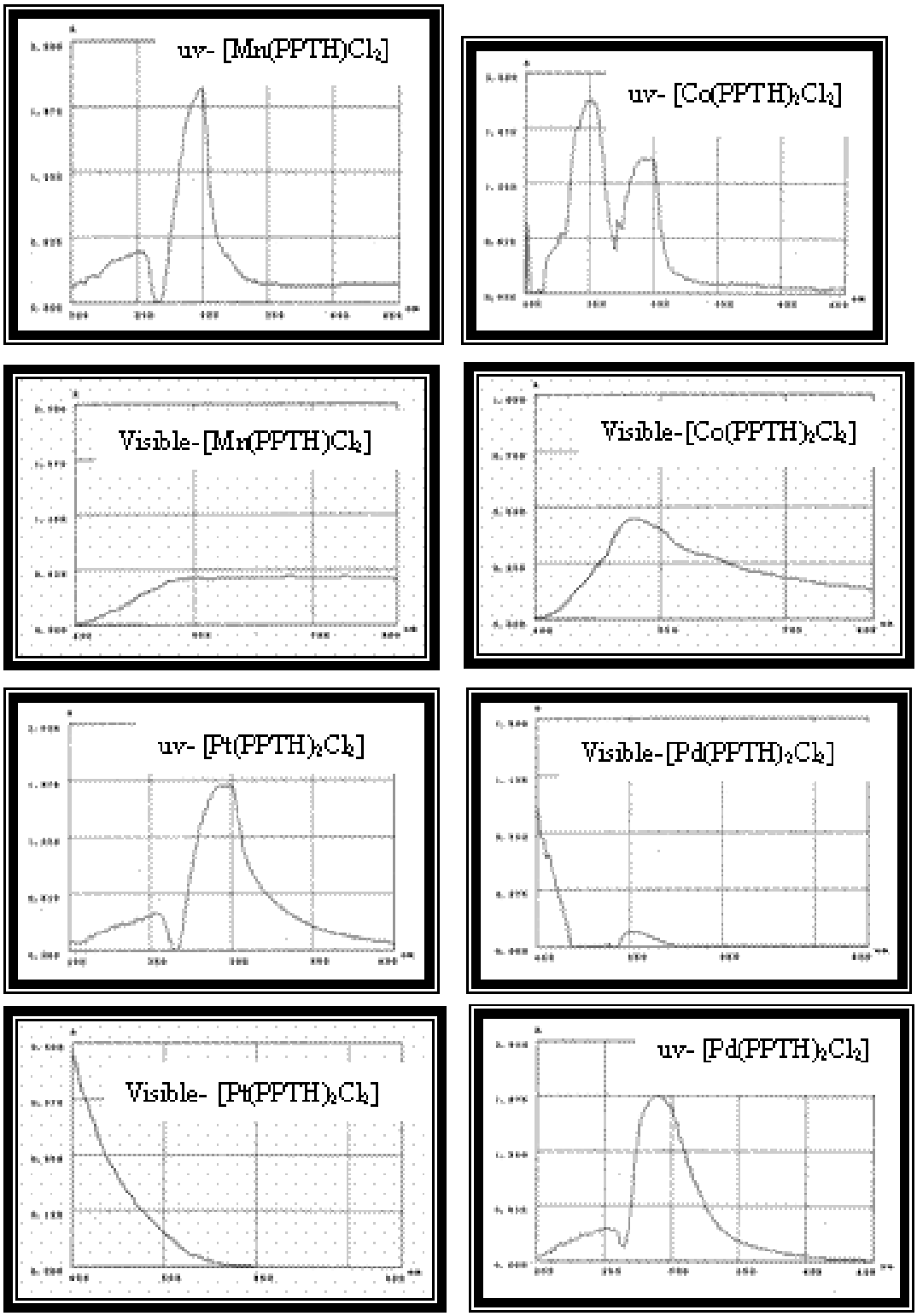

Fig. 1: Electronic spectra of $[Mn(PPTH)Cl_2]$, $[Co(PPTH)_2Cl_2]$ and $[Pt(PPTH)_2Cl_2]$

+ δ(C-H), band (III) has contribution from υ(C-N) + υ(C=S) and band (IV) has contribution from υ(C=S) [29].

The prepared metal complexes exhibit four thioamide bands. The bands in the range 1543-1585cm^{-1} which are attributed to thioamide band I are shifted to higher frequencies due to coordination of the ligand to the metal ions[18,24].

The bands in the range 1450-1487 cm^{-1}which are assigned to thioamide band II are shifted

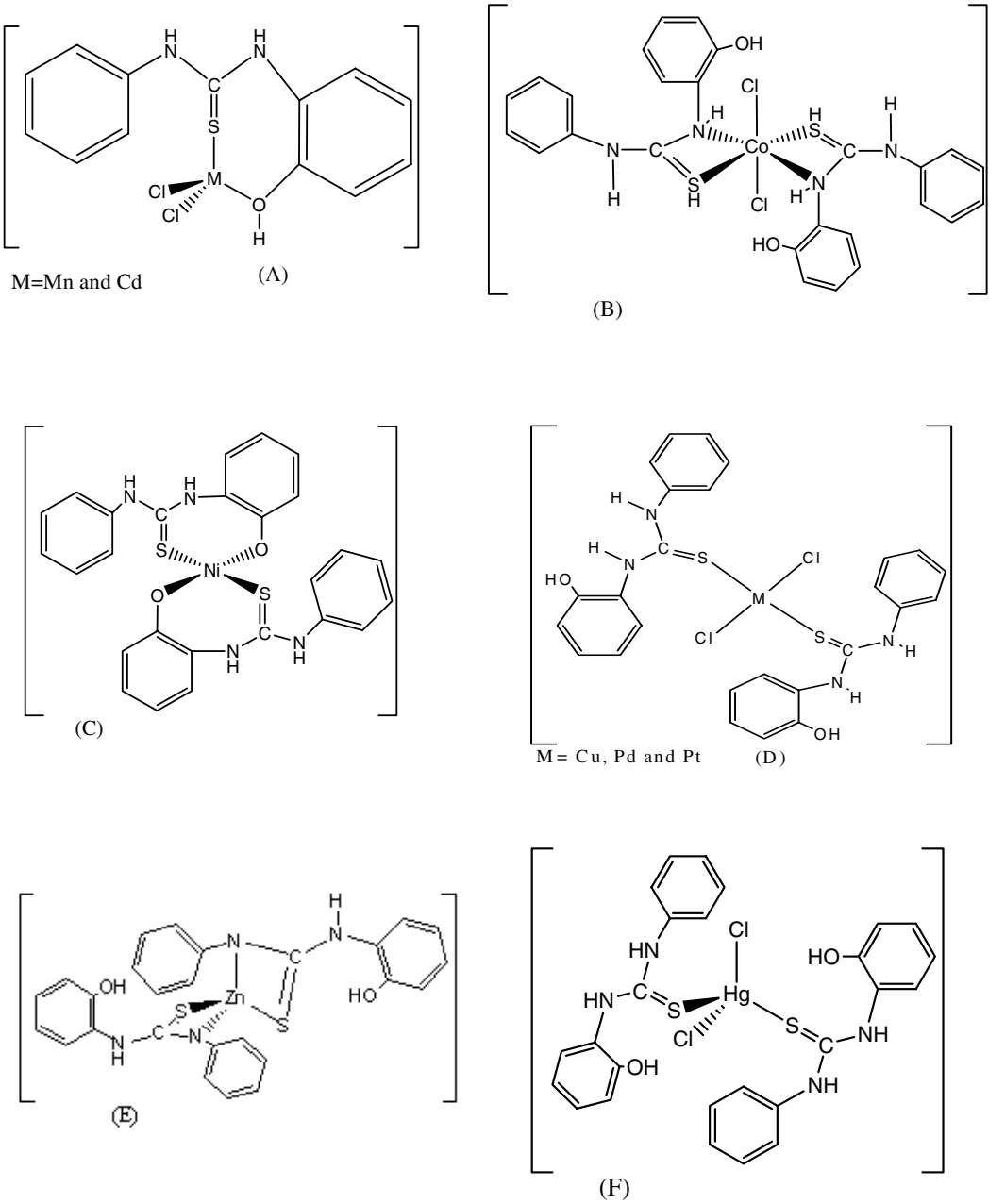

Fig. 2: Chemical structures of the prepared complexes; (A) tetrahedral [M(PPTH)Cl$_2$], (B) Octahedral [Co(PPTH)$_2$Cl$_2$], (C) Square Planar [Ni(PPT)$_2$], (D) Square Planar [M(PPTH)$_2$Cl$_2$], (E) Tetrahedral [Zn(PPT)$_2$] and (F) Tetrahedral [Hg(PPTH)$_2$Cl$_2$]

to higher frequencies due to linking of the ligand to the metal ion centers[18,24]. The bands in the range 995-1033 cm^{-1} which are attributed to thioamide band III are shifted to higher frequencies in these complexes[18].

The bands in the range 684-700 cm^{-1} which are assigned to thioamide band IV are shifted to lower frequencies in complexes 4-9, while in the complexes; 1,2 and 3 are shifted to higher frequencies[18,23]. The shifting of these four thioamide bands of the ligand to higher or lower frequencies in the complexes indicate that the ligand (PPTH) is coordinated to the metal centers in these complexes.

The infrared spectrum of the ligand (PPTH) shows a band at 3144 cm^{-1} which is attributed to υ(O-H) [30-32]. The infrared spectra of the metal complexes 1, 2, 4, 5, 6, 7, 8 and 9 show bands in the range 3140-3481 cm^{-1} which are assigned to υ (O-H) [31]. In the complexes 2, 5, 7, 8 and 9 the ligand is not coordinated through the oxygen atom of the hydroxyl group to the metal centers, while in the complexes 1, 4 and 6 the ligand is coordinated to the metal centers through oxygen atom of the hydroxyl group[33]. The absence of υ (O-H) in the complex 3 is due to the coordination of the ligand PPTH through oxygen atom of its deprotonated hydroxyl group to Ni(II) center[34-36].

The infrared spectrum of the free ligand (PPTH) show a band at 3321cm^{-1} which assigned to υ (N-H) of the secondary amine of thioureido group[30-32].

The infrared spectra of complexes; 1, 2, 3, 4, 6, 7 and 9 show bands in the range 3221-3342 cm^{-1} are assigned to υ (N-H) of the secondary amine. This indicates that the ligand is not coordinated to the metal centers through the N-atom of its secondary amine group. In complex 2 the ligand (PPTH) is coordinated to the metal centers through its nitrogen of the secondary amine group without deprotonation but its υ(N-H) band is shifted to a higher frequency[37,38]. In complex 5 the ligand (PPTH) is coordinated to the Zn(II) centre through one of its deprotonated secondary amine group and its second υ(N-H) band is disappeared due to its overlap with υ(O-H) of water[38,20].

Table 1: Color, melting point, elemental analysis and conductivity data for the synthesized PPTH and metal complexes.

No.	Compound	Yield (%)	Color	m.p.(^0C)	Found		(Calculated)%		Λm (Ω^{-1} cm^2 mol^{-1})
					C	H	N	S	
	$C_{13}H_{12}N_2OS$	45	White	139-140	63.41 (63.91)	4.97 (4.95)	11.33 (11.47)	13.19 (13.12)	1.53
1	$[MnC_{13}H_{12}N_2OSCl_2]$	57	Brown	>330 decompose	42.25 (42.18)	3.21 (3.27)	7.75 (7.57)	9.01 (8.66)	6.5
2	$[CoC_{26}H_{24}N_4O_2S_2Cl_2]$	70	Green	168-170	50.61 (50.49)	3.87 (3.91)	9.12 (9.06)	10.31 (10.37)	8.59
3	$[NiC_{26}H_{22}N_4O_2S_2]$	47	Grassy	158-160	57.33 (57.27)	4.15 (4.07)	10.24 (10.27)	11.69 (11.76)	7.74
4	$[CuC_{26}H_{24}N_4O_2S_2Cl_2]$	59	Gray	218-220	50.10 (50.12)	4.01 (3.88)	8.85 (8.99)	11.28 (10.29)	20.2
5	$[ZnC_{26}H_{22}N_4O_2S_2]$	38	White	>360	56.64 (56.57)	4.01 (4.02)	10.19 (10.15)	10.89 (11.62)	3.3
6	$[CdC_{13}H_{12}N_2OSCl_2]$	44	Yallow	>360	36.49 (36.51)	2.99 (2.83)	6.52 (6.55)	6.68 (7.50)	12.24
7	$[PdC_{26}H_{24}N_4O_2S_2Cl_2]$	88	Orange	160-162	47.01 (46.89)	3.62 (3.63)	8.58 (8.41)	10.14 (9.63)	20.8
8	$[PtC_{26}H_{24}N_4O_2S_2Cl_2]$	84	Brown	168-170	41.45 (41.38)	3.19 (3.21)	7.51 (7.42)	8.45 (8.50)	10.12
9	$[HgC_{26}H_{24}N_4O_2S_2Cl_2]$	41	White	150-152	30.23 (30.27)	2.41 (2.34)	5.39 (5.43)	6.82 (6.22)	6.63

Table 2: Selected IR bands of the PPTH and its metal complexes (cm^{-1})

No.	Compounds	Thioamide bands				O-H	N-H	M-N	M-O	M-S	M-Cl
		I	II	III	IV						
	PPTH	1543(vs)	1452(m)	995(w)	700(m)	3144(b)	3321(m)	(————)	(———)	(———)	(———)
1	$[Mn(PPTH)Cl_2]$	1574(s)	1462(w)	1024(m)	700(m)	3412(b)	3321(b)	(————)	470(w)	360(w)	312(w)
2	$[Co(PPTH)_2Cl_2]$	1585(s)	1487(m)	1033(m)	700(s)	3250(b)	3342(m)	600(w)	(———)	360(s)	330(w)
3	$[Ni(PPTH)_2]$	1564(vs)	1475(w)	1033(w)	700(s)	(———)	3325(s) 3236(s)	(————)	638(m)	350(w)	(——)
4	$[Cu(PPTH)_2Cl_2]$	1585(s)	1474(w)	1000(w)	686(m)	3198(b)	3304(w)	(————)	(——)	360(w)	270(s)
5	$[Zn(PPTH)_2]$	1543(vs)	1450(w)	1008(m)	692(s)	3343(b)	(———)	423(w)	(———)	360(w)	(——)
6	$[Cd(PPTH)Cl_2]$	1585(vs)	1464(s)	1015(m)	684(s)	3481(b)	3298(w)	3250(w)	(————)	425(w)	360(w) 248(w)
7	$[Pd(PPTH)_2Cl_2]$	1553(vs)	1454(m)	1002(w)	692(m)	3142(b)	3221(b)	(———)	(———)	359(vs)	307(m) 295(w)
8	$[Pt(PPTH)_2Cl_2]$	1547(s)	1454(m)	1033(w)	692(m)	3180(b)	(———)	(———) 290(w)	(———)	355(s)	319(m)
9	$[Hg(PPTH)_2Cl_2]$	1561(vs)	1455(s)	1002(m)	691(vs)	3140(b)	3272(b)	(———)	(———)	359(s)	310(w)

vs: very strong s: strong m: medium w: weak

The infrared spectra of the complexes 1, 3, 4, 6, 7, 8 and 9 have no υ (M-N) bands. This means that the ligand is not coordinated to the metal centers through its N-atoms of the secondary amine group while the complexes 2 and 5 have bands at 600 cm^{-1} and 423 cm^{-1} respectively. which are attributed to υ (M-N) vibration which means that the ligand is coordinated to the metal centers through N-atom of its secondary amine group[39,40]. The infrared spectra of the complexes 2, 5, 7, 8 and 9 show no υ (M-O) bands which means that the ligand is not coordinated to the metal centers through O-atom of its phenolic hydroxyl.The complexes 1, 3 and 6 have bands at 470 cm^{-1}, 639 cm^{-1}, 405 cm^{-1} and 425 cm^{-1} respectively which are assigned to υ (M-O), this indicates that the ligand is coordinated to the metal centers through oxygen atom of its phenolic OH [36,39,40,41].

The infrared spectra of all complexes 1-9, show bands in the range 330-360 cm^{-1} which are attributed to υ (M-S) vibrations[38,21]. This means that the ligand is coordinated to the metal centers through S-atom of its thioamide group. The infrared spectra of the complexes 1, 2, 4, 6 and 9 show bands at 330 cm^{-1}, 270 cm^{-1}, 248 cm^{-1} and 310 cm^{-1} respectively which are assigned to υ(M-Cl) vibration in these complexes[21,42,43]. The infrared spectrum of the Pd(II) complex show two bands at 307 cm^{-1} and 295 cm^{-1} which are assigned to υ(Pd-Cl) in cis geometry [23]. Also Pt(II) complex has two infrared bands at 319 cm^{-1} and 290 cm^{-1}which are attributed to υ (Pt-Cl) in cis-geometry[23].

Electronic spectra

The electronic spectrum of complex 1 shows two bands in uv-visible region at 33445 cm^{-1} and 40000 cm^{-1}, Table (3), figure (1), which are denoted to Mn-ligand charge transfer transition[44].

The electronic spectrum of the complex 2, show bands at 34364 cm^{-1}, 40323cm^{-1} and 19493 cm^{-1} , Table (3), figure (1) the bands at 34364 cm^{-1} and 40323 cm^{-1} are assigned to charge transfer transitions[23], while the band at 19493 cm^{-1} is assigned to transition $^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$ of Co(II) in an

Table 3: Electronic spectral bands and magnetic susceptibility of the prepared complexes from PPTH

No.	Complex	ε×10³	Band absorption cm^{-1}	nm	Assignment	μeff (B.M)
	PPTH	2.05	35971	276		
1	$[Mn(PPTH)Cl_2]$	8.232	33445	299	C.T	5.9
		2.1	40000	250	C.T	T.d.
2	$[Co(PPTH)_2Cl_2]$	61.2	34364	291	C.T	3.7
		88	40323	248	C.T	Oh
		o.446	19493	513	$^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$	
3	$[Ni(PPTH)_2]$	135.12	34362	291	C.T	0.02
		30.8	39370	254	C.T	Sq.pl
4	$[Cu(PPTH)_2Cl_2]$	114.96	33445	299	C.T	1.77
		16.8	39370	254	C.T	Sq.pl
5	$[Zn(PPTH)_2]$	21.58	33333	300	C.T	Diamagnetic T.d.
		2.98	44643	224	C.T	
6	$[Cd(PPTH)Cl_2]$	18.056	33333	300	C.T	Diamagnetic T.d.
		3.08	39370	254	C.T	
7	$[Pd(PPTH)_2Cl_2]$	60.51	34722	288	C.T	Diamagnetic
		12.3	39526	253	C.T	Sq.pl
8	$[Pt(PPTH)_2Cl_2]$	58.272	33670	297	C.T	Diamagnetic
		13.44	39683	252	C.T	Sq.pl
9	$[Hg(PPTH)_2Cl_2]$	15.936	33898	295	C.T	Diamagnetic T.d.
		3.64	39683	252	C.T	

octahedral arrangement[23,45]. The electronic spectrum of the complex 3, show bands at 34362 cm^{-1} and 39370 cm^{-1} which denote to Ni-ligand charge transfers[23]. The electronic spectrum of the complex 4, show bands at 33445 cm^{-1} and 39370 cm^{-1} which denotes to Cu-ligand charge transfer[23]. The electronic spectra of Zn, Cd and Hg complexes show electronic transitional bands in the range 33333-44643 cm^{-1} , Table (3), which are either assigned to charge transfer or internal ligand transitions[23]. The electronic spectra of complexes 7 and 8, show bands in the range 33670-39683cm^{-1} which are attributed to charge transfer transitions, Table (3), figure (1)[24].

Magnetic susceptibility

The magnetic susceptibility of synthesized complexes are shown in Table (3). The magnetic susceptibility of Mn(II) complex, 1, is 5.9 B.M., which confirms a tetrahedral geometry around Mn(II)[46]. The magnetic susceptibility of Co(II) complex, 2, is 3.7 B.M. which denotes to an octahedral geometry around Co(II)[47].The magnetic susceptibility of Ni(II) complex, 3, is 0.02 B.M. which indicates a square-planar geometry around Ni(II)[48]. The magnetic susceptibility of Cu(II) complex, 4, is 1.77 B.M. which suggests a square-planar arrangement around Cu(II)[39]. The magnetic susceptibility of Pd(II) and Pt(II) complexes 7 and 8, are zero, which indicate that these complexes are diamagnetic and have square-planar geometries around metal centers[45]. The magnetic susceptibility of Zn(II), Cd(II) and Hg(II) are zero which denote to that they are diamagnetic and have tetrahedral arrangements around metal centers[39,49].

Biological of the ligand (PPTH) and its metal complexes

The measured biological activities of the ligand (PPTH) and its metal complexes are arranged in Table (4). The ligand (PPTH) is resistant against these three bacteria (Escherichia coli, Pseudomonas aeruginosa and Staphylococcus aureus). The complexes 3, 5 and 9 are sensitive against Escherichia coli bacterium while the other complexes are resistant.

The complexes 4 and 7 are sensitive against Staphylococcus aureus bacterium while the complex 6 is highly sensitive against this bacterium, but the other complexes are resistant.The complexes 1-9 are resistant against Pseudomonas aeruginosa bacterium. It is concluded that the activity of the PPTH ligand is enhanced when it is coordinated to some of these metal centers.

According to elemental analysis, IR and uv-visible spectroscopy, conductivity and magnetic susceptibility data the following structures are proposed for the synthesized metal complexes as shown in figure (2) .

Table 4: Biological activity of ligand (PPTH) and its metal complexes

No.	Compound	*Escherichia coli* Gram(-)	*Pseudomonas aeruginoses* Gram(-)	*Staphylococcus aureus* Gram(+)
	PPTH	R	R	R
1	$[Mn(PPTH)Cl_2]$	R	R	R
2	$[Co(PPTH)_2Cl_2]$	R	R	R
3	$[Ni(PPTH)_2]$	S	R	R
4	$[Cu(PPTH)_2Cl_2]$	R	R	S
5	$[Zn(PPTH)_2]$	S	R	R
6	$[Cd(PPTH)Cl_2]$	R	R	S*
7	$[Pd(PPTH)_2Cl_2]$	R	R	S
8	$[Pt(PPTH)_2Cl_2]$	R	R	R
9	$[Hg(PPTH)_2Cl_2]$	S	R	R

R: Resistant S: Significant S*: High significant

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