Synthesis and Characterization of Bimetallic Complexes of the type $[L_2Pd(\mu\text{-dppm})_2MX_n]$; (MX_n = $MnCI_2$,$CuCl_2$, $PtCI_2$, $PdCl_2$, $SnCI_4$ and $Mo(CO)_4$, L = deprotonated 4 , 5- diphenyl- 1,2,4- triazole-3-thione and dppm = bis(diphenylphosphino)methane

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Abstract

Treatment of cis-[PdL_2] with dppm (1:2) gave the complex [$PdL_2(dppm)_2$] . Reaction of the [$PdL_2(dppm)_2$] with some transition metals in chloroform yielded bimetallic complexes of the type [$L_2Pd(\mu\text{-dppm})_2MX_n$] ; where (MX_n = $MnCI_2$,$CuCl_2$, $PtCI_2$, $PdCl_2$, $SnCI_4$ and $Mo(CO)_4$) . The prepared bimetallic complexes were characterized by elemental analysis , infrared , UV./ Vis. , molar conductance , magnetic susceptibility measurement .

Keywords: Triazole complexes, diphosphine complexes, bimetallic complexes, palladium(II) and platinum(II)complexes.

الخلاصة

معاملة cis-[PdL_2] مع dppm بنسبة (2:1) اعطت المعقد [$PdL_2(dppm)_2$] . كذلك تفاعل المعقد
[$PdL_2(dppm)_2$] مع بعض عناصر انتقالية فى الكلوروفورم اعطت معقدات ثنائية الفلز من نوع
[$L_2Pd(\mu\text{-dppm})_2MX_n$] : حيث ان
(MX_n = $MnCI_2$,$CuCl_2$, $PtCI_2$, $PdCl_2$, $SnCI_4$, $Mo(CO)_4$).
تم تشخيص معقدات ثنائية الفلز المحضرة بواسطة التحليل الدقيق للعناصر و اطياف IR و UV./ Vis.
وتوصيل الكهربائى المولي وقياسات الحساسية المغناطيسية.

Introduction

Great interest has been devoted to dppm because of its small bite, often to bridge rather than chelate [1].The use of dppm or chelated ligands in the construction of bimetallic and trimetallic complexes has developed tremendously over the last 20 years and a number reviews of this area have appeared[2-8]. The dppm bridged complexes of platinum or palladium have received considerable attention including A-Frame species that contain a bridging group such as CH_2 , CO, SO_2 or another metal [9,10] due to their extensive uses as catalysts [11-14]. .Also phosphine metal complexes are potential antitumor agents and have shown antitumor activity against a wide range of tumors [15]. Fused and pendant 1,2,4-triazoles are a ubiquitous feature of many pharmaceutical and agrochemical products [15] . Some other 1,2,4-triazole and 1,3,4-thiadiazole heterocyclic entities that are very interesting components in term of their biological properties such as antifungal [16] , antibacterial [17] , herbicidal [18] and plant growth regulater activities have been reported [19]. It is expected that

1,2,4-triazole -3-thione may act in synergetic fashion with bridged dppm in bimetallic complexes to give bifunctional antitumor agents and potential precursors for polymeric complexes.

In this paper we report for the first time , the synthesis and characterization of bimetallic complexes of Pd(II) , Pt(II) , Mn(II) , Cu(II) , Sn(IV) and $Mn(CO)_4$ containing bridging dppm and pendant mercaptotriazoles.

2- Experimental

2-1. General

Infrared spectra were recorded on a PYE-Unicam Sp3-300s spectrophotometer in the range 200-4000 cm-1 using cesium iodide discs. Elemental analysis were carried out on a Carlo Erba type 1106 CHN analyzer. Conductivity measurements were made on 10^{-3} M solutions of the complexes in chloroform at ambient temperature using CCMD 625 COMBINED ONDUCTIVITY / PM WPA conductivity meter. Electronic spectra were recorded on a Jenway 6485 spectrometer for 10^{-3} M solutions of the complexes in chloroform at room temperature using a 1cm quartz cell. Magnetic measurement data were recorded on Brucker BM6 instrument at ambient temperature following Faraday method. Melting points were measured using Toshinwall-Electrothermal melting point apparatus.

2.2. Starting materials

Bis(diphenylphosphino)methane, phenylisothiocyanate, stannic(IV)chloride–pentahydrate and molybdenum hexacarbonyl were obtained from Fluka. Hydrazinehydrate, ethylbenzoate, piperidine, palladium(II)chloride, copper(II)chloride-dihydrate, manganese(II)chloride dehydrate and hexachloroplatinic acid were purchased from BDH . All the reagents were used as received. The deprotonated ligand 4 , 5-diphenyl-1, 2 , 4-triazole-3-thione (L) [20], cis-[$PtCI_2$ $(DMSO)_2$][21] , K_2PtCI_4 [22] , Na_2PdCI_4 [23] and Cis- [PdL_2] [24] were prepared as described in literature cited.

2.3. [$PdL_2(dppm)_2$]

A solution of dppm ($7.5x10^{-2}$ g , 0.1965mmol) in $3cm^3$ chloroform was added to a clear red – colored solution of cis-[PdL_2] (0.06g , 0.0983 mmole) in 5 cm^3 chloroform to give a clear red solution which was heated on steam bath for 8 minutes to give a clear red-orange solution.The red-orange solution left overnight for solvent evaporation at room temperature and an orange precipitate was left.Then the precipitate was dissolved in dichloromethane and allowed to stand at room temperature for evaporation to give an orange powder.(yield, 95%)

2.4. [$L_2Pd (dppm)_2 MnCl_2 (H_2O)_2$]

Solid $MnCl_2 .2H_2O$ ($1.11x10^{-2}$g , 7.25x 10^{-2} mmol) was added to a a clear orange solution of cis-[PdL_2 $(dppm)_2$] (0.05 g , $3.62x10^{-2}$ mmole) in CH_2Cl_2 /EtOH (2:1) $12cm^3$. The mixture was heated on water-bath with stirring for ten minutes to give a red-orange solution. The resulting red-orange solution was heated on steam bath until its volume reduced to half, then cooled to room temperature. On addition of diethylether to the solution a yellow precipitate formed which was separated from the solution using Hirsch funnel . Finally the precipitate. Was washed with D.W. and its color changed to orange and left to dry at room temperature. (yield 26%) .

2.5. [L_2Pd $(dppm)_2$ $CuCl_2$]

Solid $CuCl_2$ $2H_2O$ ($1.23x10^{-2}$ g ,$7.2547X10^{-2}$ mmol) was added to a clear orange solution of cis- [PdL_2 $(dppm)_2$] ($3.6273x10^{-2}$ mmol) in CH_2Cl_2 /EtOH (2:1) 12 cm^3. The deep colored mixture was heated on steam-bath with stirring for seven minutes then cooled to room temperature . Diethylether was added to the deep colored mixture and a brown-yellowish precipitate was formed immediately, The precipitate was allowed to settle and then separated by decantation. Finally the precipitate was dried at room temperature to give an olive colored powder(yield 42%).

2.6. [L_2 Pd($(dppm)_2$ $SnCl_4$]

Solid $SnCl_4$.$2H_2O$ ($2.54x10^{-2}$ g ,$7.2547X10^{-2}$ mmol) was added to a clear orange solution of cis-[PdL_2 $(dppm)_2$] ($3.6273x10^{-2}$ mmol) in CH_2Cl_2 /EtOH (2:1) 12 cm^3 to give a clear yellow-orange solution .The solution was heated on steam-bath with stirring for five minutes then left to cool to room temperature .Then Diethylether was added to the cooled solution to give a greenish-yellow solution which was left an overnight at room temperature for evaporation and a yellow solid powder was obtained (yield 98%).

2.7. [L_2 Pd $(dppm)_2$ $PtCl_2$]

Solid cis-[Pt $(DMSO)_2$] ($1.83x10^{-2}$ g , 4.3339 x 10^{-2} mmole) was added to a clear orange solution of cis-[PdL_2 $(dppm)_2$] (0.06g , $4.3528x10^{-2}$ mmole) in chloroform 12 cm^3 to give a clear solution .The resulted solution was heated on steam-bath until its volume reduced to half and its color turned to orange-yellow .the orange-yellow solution was evaporated to dryness at room temperature to give an orange yellow powder which finally washed with diethylether and dried.(yield 63%).

2.8. [L_2 Pd $(dppm)_2$ $PdCl_2$]

A solution of cis-[$PdCl_2$ $(DMSO)_2$] ($1.693x10^{-2}$g, $5.0783x10^{-2}$ mmol) in chloroform 5cm^3 was added with stirring to a solution of the cis-[$Pd(TR)_2$ $(dppm)_2$]($5.0783x10^{-2}$ mmol) in chloroform 7 cm^3 to give a clear yellow orange solution . The resulted solution was heated on steam-bath until its volume reduced to half and its color turned yellow. The yellow solution was cooled to room temperature and diethylether was added till a yellow precipitate formed which was allowed to stand for two hours for complete separation of the yellow ppt. Finally the yellow precipitate separated from the solution by decantation and dried at room temperature.

(yield 63%) .

2.9. [L_2 Pd $(dppm)_2$ Mo($CO)_4$]

A solution of [Mo $(CO)_4$ $(pip)_2$] ($1.92x10^{-2}$ g ,$5.0783x10^{-2}$ mmol) in dichloromethane 5cm^3 was added to a solution of the cis- [$Pd(TR)_2$ $(dppm)_2$] ($5.0783x10^{-2}$ mmol) in dichloromethane 7 cm^3 and stirred for ten minutes to give a dark -red solution .The dark-red solution left in a dark place at room temperature for evaporation to give an orange powder. Finally to a solution of the orange powder in minimum volume of dichloromethane , n-hexane was added and left an overnight for evaporation at room temperature to give a yellow powder . (yield 55.83 %) .

3- Results and Discussion

3-1 Square planar – [pdL$_2$(dppm)$_2$]

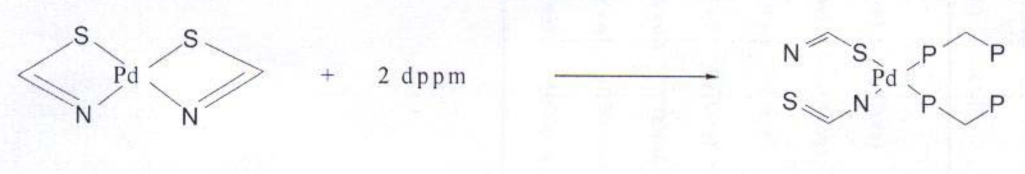
The reaction of the complex cis-[pdL$_2$] with dppm in the mole ratio (1:2) in chloroform yielded an orange complex of the formula square planar-[pdL$_2$(dppm)$_2$]cis[pdL$_2$]+2dppm $\longrightarrow$ square planar-[pdL$_2$(dppm)$_2$].

The complex is soluble in chloroform and dichloromethane but insoluble in water and diethyl ether. Elemental analysis data, Table(1), of this complex confirms the suggested formula. Conductivity measurement, Table(1), indicates that it is non-electrolyte.

Table (1): Color, melting point, elemental analysis and conductivity data for the prepared complexes

No.	Complexes	Color	Found (cacld.) %				
			m.pC^0	C	H	N	$\Delta\ \Omega^{-1}\ cm^2\ mol^{-1}$
1	cis-[Pd (L) $_2$]	deep red	268-275	54.66(55.04)	3.19(3.27)	13.48(13.76)	1.4
2	[Pd (L $_2$(dppm) $_2$]	orange	174-176	67.60(67.9)	4.55(4.64)	6.12(6.09)	3.05
3	[L $_2$Pd (μ-dppm)$_2$MnCl$_2$ (H$_2$O)$_2$]	orange	188-191	63.01(62.22)	4.32(4.25)	5.70(5.58)	3.2
4	[L $_2$Pd (μ-dppm$_)2$CuCl$_2$]	olive	238-240	60.05(6186)	4.12(4.23)	4.98(5.55)	0.3
5	[L $_2$Pd (μ-dppm)$_2$SnCl$_4$]	Yellow	242-244	57.35(57.10)	3.87(3.90)	5.44(5.12)	0.5
6	[L $_2$Pd (μ-dppm)$_2$PtCl$_2$]	orange yellow	258-260	57.74(56.92)	3.70(3.89)	5.21(5.10)	1.3
7	[L $_2$Pd (μ-dppm)$_2$PdCl$_2$]	yellow	256-257	60.36(60.16)	4.35(4.11)	5.56(5.39)	3.5
8	[L)Pd(μ-dppm)$_2$Mo(CO)$_4$]	yellow	164-166	59.84(62.02)	4.21(4.28)	5.44(5.29)	2.6

The infrared spectrum of the square planar-[PdL$_2$(dppm)$_2$], Figure(1), shows two bands at 430 cm^{-1} and 1070cm^{-1} which are attributed to ν(Pd-P)[25] and ν(C-P)[26] respectively indicating that the dppms are coordinated to the Pd(II). There are no significant shifts in the thioamide bands position, Table(2), indicating that the trizole ligands are still linked to the metal in the square planar-[PdL$_2$(dppm)$_2$].



Sq.pl.- [PdL$_2$]

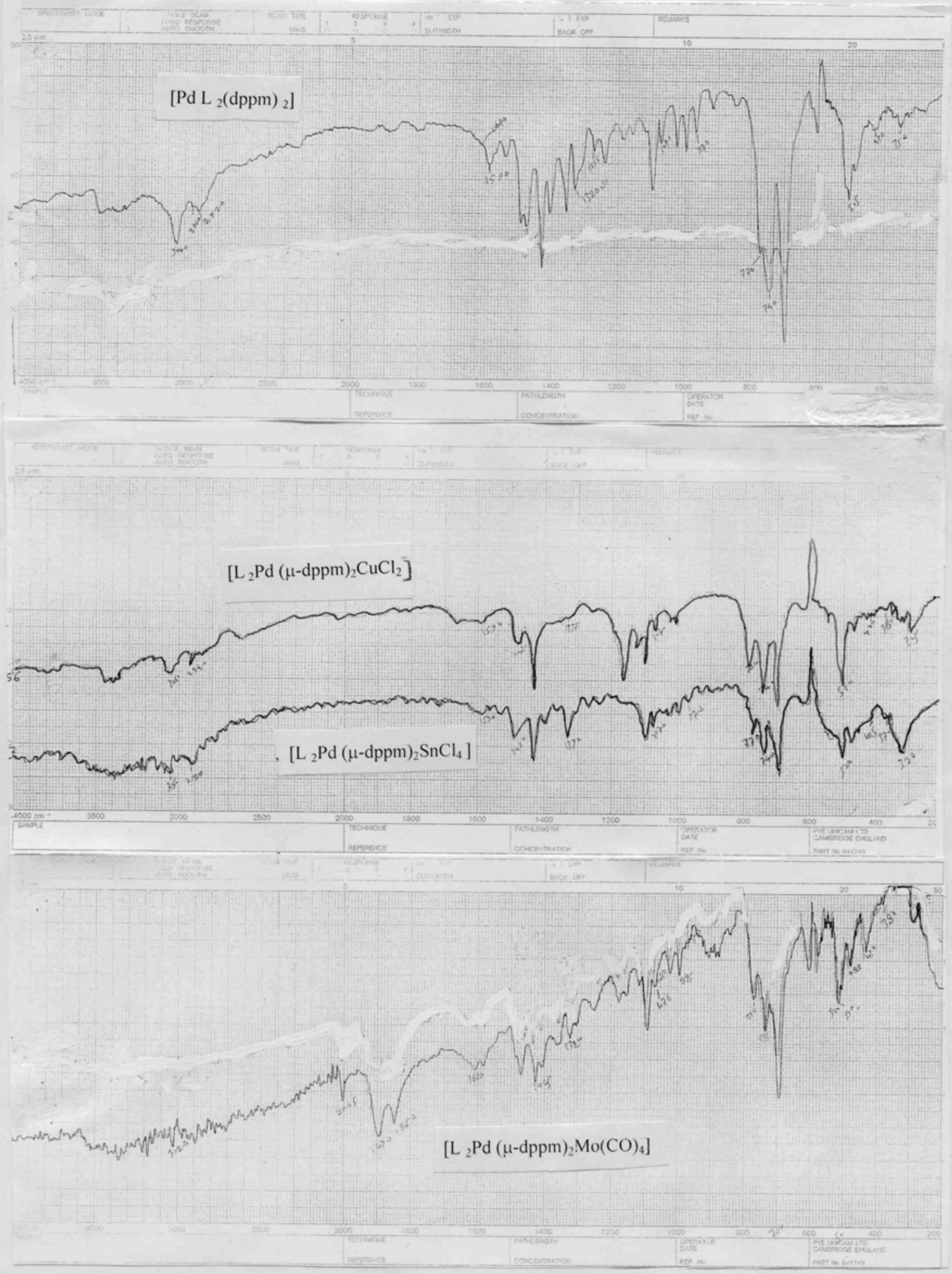
Sq.pl.- [PdL $_2$ (dppm)$_2$]

Magnetic susceptibility measurement, Table(3), showed that the complex is diamagnetic suggesting a square planar structure [27]. The electronic spectrum of the complex, Figure(2) showed two bands at 40650 cm^{-1} and 44843 cm^{-1} which are charge transfer bands [28].

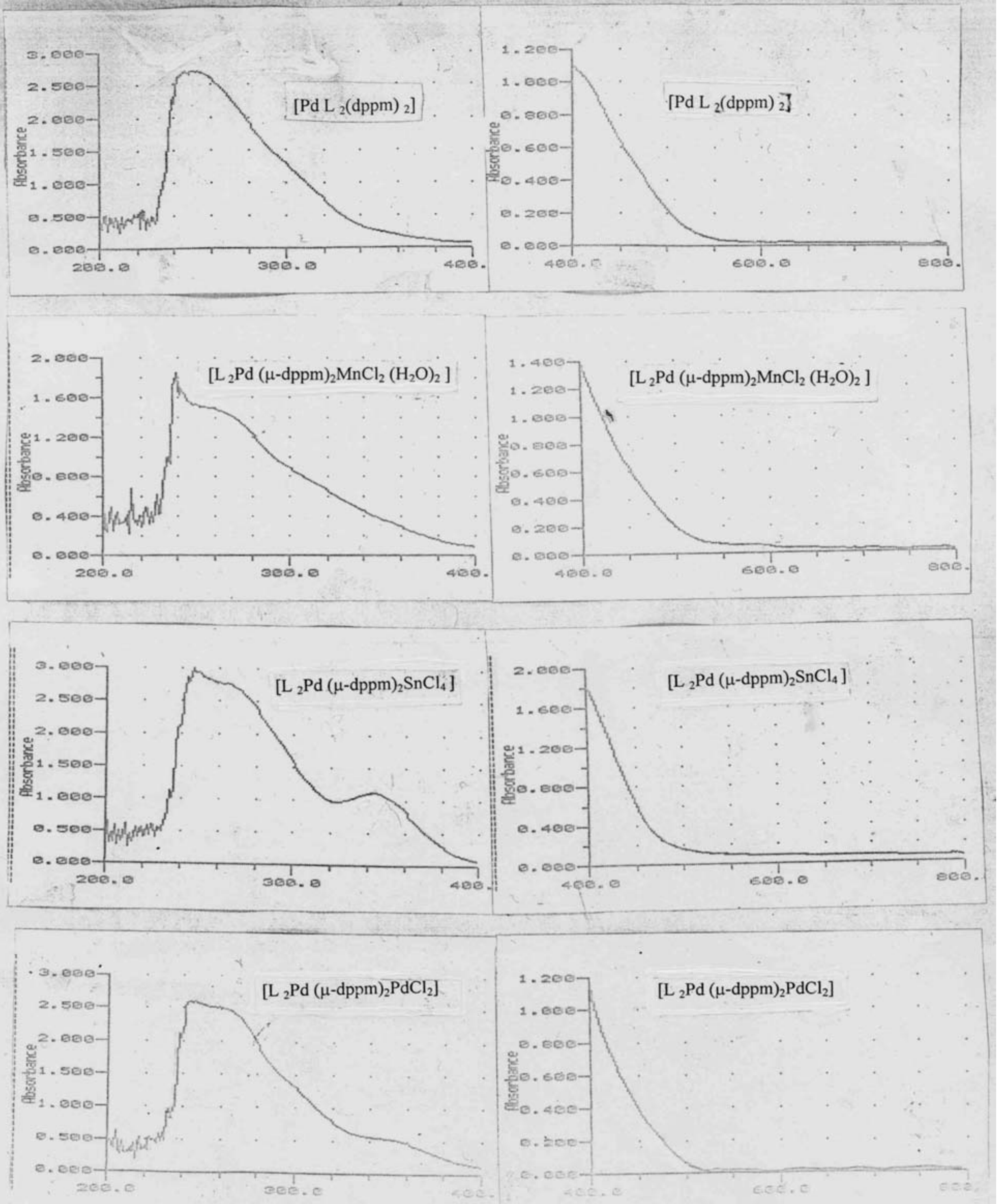
Table (2) Selected IR bands of the mercaptotriazole complexes (cm^{-1})

complex	Thioamide bands												
No.	I	II	III	IV	ν (C-H)	ν(M-N)	ν(M-S)	ν(M-C)	ν(M-P)	ν(C-P)	ν(N-N)	ν(O-H)	ν(C-O)
1	1588(s)	1320(s)	965(s)	770(vs)	3040(m)	520(m) 480(m)	380(m) 455(m)	-	-	-	1465(m)		
2	1590(m)	1320(s)	970(m)	770(vw) 740 (vs)	2960(w) 3040(m)	550(vs)	350(m)	-	430(w)	1070(s)	1475(s)	-	
3	1620(w)	1332(s)	975(s)	780 (m) 750 (m)	2960(w) 3040(w)	510(s)	370(w)	-	430(w)	1070(sh)	1480(m)	3400b	
4	1590(w)	1335(w)	-	780 (m) 745 (s)	3060(w) 2940(w)	510(vs)	380(w)	305(m)	420(w)	1075(w)	1480(m)	-	
5	1590(w)	1330(s)	970(m)	770 (w) 740 (s)	2920(w) 3050(w)	500(s)	370(vw)	320(s)	415(w)	1070(w)	1490(m)	-	
6	1590(vw)	1325(m)	970(m)	780 (w) 740 (s)	2900(w) 3050(w)	510(s)	360(w)	290(m) 315(m)	440(vw)	1070(vw)	1475(m)	-	
7	1610(w)	1330(m)	-	770 (w) 735 (s)	2920(w) 3040(w)	510(s)	370(w)	290(m) 302(s)	440(vw)	1070(vw)	1480(s)	-	
8	1610(w)	1315(w) 1330(w)	970(w)	770 (s) 735 (s)	2920(w) 3005(w)	520(s)	380(w)	-	430(s)	1070(vw)	1480(s)	-	2010 (m) , 1910 (m) 1900 (s) , 1855 (s)

S= strong, vs= very strong, w=weak, vw= very weak, m= medium, sh= shoulder



Figure(1) : Infrared spectra of some of the prepared complexes : [Pd L $_2$(dppm) $_2$] , [L $_2$Pd (μ-dppm)$_2$CuCl$_2$], (L $_2$Pd (μ-dppm)$_2$SnCl$_4$] and [L $_2$Pd (μ-dppm)$_2$Mo(CO)$_4$]



Figure(2) :Electronic spectra of some of the prepared complexes : [Pd L $_2$(dppm) $_2$] , [L $_2$Pd (μ-dppm)$_2$MnCl$_2$ (H$_2$O)$_2$] , [L $_2$Pd (μ-dppm)$_2$SnCl$_4$] and [L $_2$Pd (μ-dppm)$_2$PdCl$_2$]

Table (3) Electronic spectral bands and magnetic susceptibilities of the prepared complexes

Complex No.	Absorption bands (cm^{-1})	Assignments	Meff(B.M)
1	39216	CT	
	27777	$^{1}A_{1}g \longrightarrow {}^{1}Eg$	Diamagnetic
	24570	$^{1}A_{1}g \longrightarrow {}^{1}B_{1}g$	Pd (11) sq.p1
	22124	$^{1}A_{1}g \longrightarrow {}^{1}A_{2}g$	
2	44843	CT	Diamagnetic
	40650	CT	Pd (11) sq.pl.
3	44843	CT	5.0
	41493	CT	Pd (11) sq.pl.
			Mn(11)Oh .=5
4	44053	CT	1.59
	40984	CT	Pd (11) sq.pl.
	28901	$^{1}A_{1}g \longrightarrow Eg$	Cu(11)sq.pl = 1.59
5	44444	CT	0
	40650	CT	Pd (11) sq.pl.
	29155	$^{1}A_{1}g \longrightarrow Eg$	Sn(1V)Oh.
6	40000	CT	0
	38022	CT	Pd (11) sq.pl.
			Pt(11)sq.pl
7	40984	CT	0
	37453	CT	Pd (11) sq.pl.
8	40816	CT	8.51
	28011	$^{1}A_{1}g \longrightarrow Eg$	Pd (11) sq.p1
	26110	$^{1}A_{1}g \longrightarrow {}^{1}B_{1}g$	Mo (0) Oh. =851

sq.pl = square planar

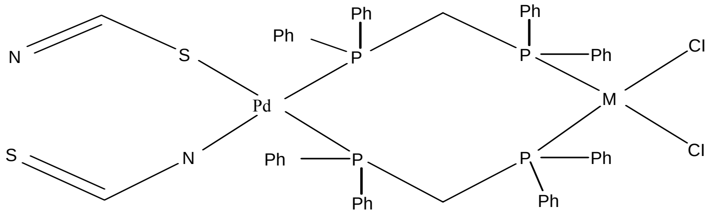
3.2. Bimetallic complexes

The elemental analysis data , Table (1), for the prepared bimetallic complexes are in a good agreement with the suggested formula. The molar conductivities , Table (1), indicate that all of these bimetallic complexes are non-electrolytes [29].

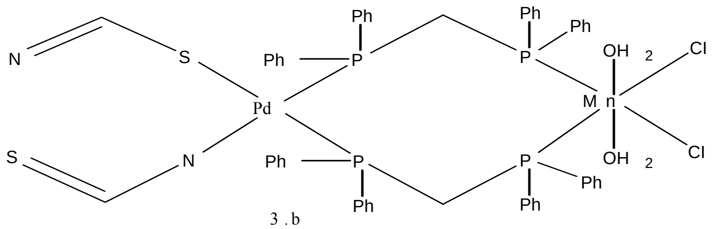
The infrared spectra of the prepared bimetallic complexes ,Figure(1), are measured in the range 200 – 4000 cm^{-1} using CsI discs and the main characteristic bands are arranged in Table(2). The bands at 1590-1620, 1315-1330 , 970-975 and 735-780 cm^{-1} are assigned to the thioamide vibrational bands I-IV respectively [30 ,31]. These thioamide bands I-IV showed no marked shifts relative to the starting complex sq.pl- [$PdL_2(dppm)_2$] which indicates that the ligands L are still coordinated to Pd(II) ion in bimetallic complexes. The bands due to vibrations of C-H , N-N , C-P and metal -N or –P or –S are in well agreement with the reported values [32]. The medium to strong vibrational bands in the 290-320 cm^{-1} range are attributed to ν (M-CI) [33-36]. The ir spectrum of the complex [L_2Pd (dppm)$_2$ $MnCl_2$ (H_2O)$_2$] showed a broad band at 3400 cm^{-1} which is assigned to ν(O-H) of H_2O [37]. The $Mo(CO)_4$ unit in the complex (8) has a local C_{2V} symmetry with the ν (CO) stretching bands at 2010 , 1910 , 1900 , and 1855 cm^{-1} are assigned to the vibrational modes $2A_1 + B_1 + B_2$ [38]. The electronic spectral data of the bimetallic complexes (3-8) ,Table (3) , are in good agreement with suggested geometries for the four coordinated Pd(II) and Pt(II) square planars[39] and six coordinated octahedral Mn(II) [40] , Sn(IV) [41] and Mo(0).

The magnetic Suceptibility values for the complexes (3) and (8) are (5.0 and 8.51 B.M.) respectively suggesting an octahedral arrangement around Mn(II) and Mo(0) [42]. The magnetic susceptibility of the complex (4) is 1.59 B.M. suggesting a square planar geometry around Cu(II)[43].

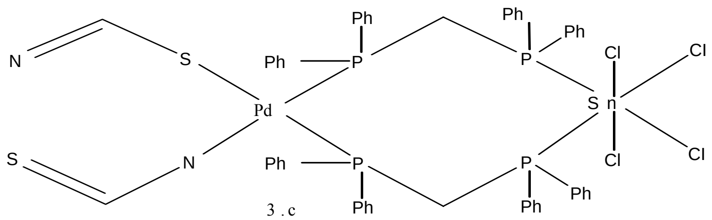
On the basis of elemental analysis data, molar conductivity , magnetic measurements, infrared\and electronic spectral data, the following structures, Figure(3), were proposed for the ynthesized bimetallic complexes .



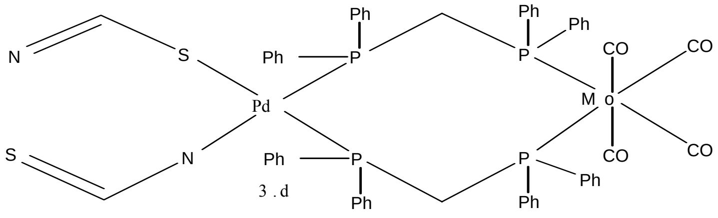
3.a Where: M = Cu(II), Pt(II), Pd(II)



3.b



3.c



3.d

Figure (3): Chemical Structures of the prepared bimetallic Complexes :

3.a [$L_2Pd(\mu\text{-dppm})_2CuCl_2$] , [$L_2Pd(\mu\text{-dppm})_2PtCl_2$] and [$L_2Pd(\mu\text{-dppm})_2PdCl_2$] ,

3.b [$L_2Pd(\mu\text{-dppm})_2MnCl_2(H_2O)_2$] 3.c [$L_2Pd(\mu\text{-dppm})_2SnCl_4$] and 3.d . [$L_2Pd(dppm)_2Mo(CO)_4$]

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