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Synthesis and characterization of some new dinuclear complexes of Ni(II) , Pd(II) and Pt(II) with bulky substituted thioether ligands

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Abstract

A series of new multidentate ligands (L^1-L^4) , 1,1,2,2-*tetrakis* [2-(benzylthio)ethylthio]ethylene(L^1),1,1,2,2-*tetrakis* [2-(*o*-tolylthio) ethylthio]) ethylene (L^2) , 1,1,2,2-*tetrakis* [3-(*p*-chlorophenylthio) ethylthio] ethylene (L^3) and 1,1,2,2-*tetrakis* [2-(*o*-aminophenylthio) ethylthio] ethyene (L^4) were prepared from the reaction of equimolamar amount of (4-mercapto-2-thia-1-butyl benzene or *o*-methyl-4-mercapto-1-thia-1-butyl benzene or p-chloro-4-mercapto-1-thia-1-butyl benzene or *o*-amino-4-mercapto -1-thia-1-butyl benzene and KOH) with tetrachloroethylene in (4:4:1) molar ratio . Reaction of the above ligands with nickel (II) , palladium (II) and platinum (II) chloride salts gave the complexes of the general formulas : $[M_2(L)Cl_4]$ and $[Ni_2(L)Cl_2]Cl_2$ M=Ni(II) , Pd(II) and Pt(II) , L=L^1-L^4 . The synthesized ligands have been characterized on the basis of their elemental analysis , FTIR, ^1H ,^{13}C NMR , and their complexes were characterized by elemental analysis metal content, UV-Vis . spectroscopic technique ,conductivity measurements and magnetic measurements.

On the basis of these studies , a four coordinate tetrahedral or square planar geometry around the metal ions in the complexes has been proposed .
Keywords : bulky substituted thioether , Ni(II) , Pd(II) [1], Pt(II) complexes , square planar complexes .

1. Introduction

A large number of dinucleating ligands containing thiophenolate subunits have been reported in the past several years [1-3]. These ligands represents soft analogues of the more familiar phenolate systems , and offer the potential of forming dinuclear complexes of catalytically active soft late transition metal ions such as Rh , Ir , Pd and Pt [4-5] . In order to enhance the affinity for these metal ions further soft donor may be introduced into the

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ligand backbone . Among these , Phosphane functions , R_2P or RS^- , are immediately evident , because these bind very strongly to the late 4d and 5d elements [6-7].

4,5-disulfanyl-1,3-dithiole-2-thionate ($dmit^{2-}$) has been used extensively for preparation of mononuclear bis-dmit and tris-dmit complexes of transition and main group metals . These sulfur rich molecules have the potential for novel electronic properties owing to the extensive π-overlap of the sulfur and metal based d-orbitals [8-9]

The two new bis-alkylpyridyl substituted dmit ligands , 4,5-bis(2-pyridylmethylsulfanyl)-1,3-dithiole-2-thione (bpmdmit), and 4,5-bis(2-pyridylmethylsulfanyl)1,3-dithiole-2-thione(bpedmit) and some of their transition metal complexes have been prepared . Two basic structural types for the complexes $[MX_2L]$, (M=Ni,Co,Cu,Pd,L=bpmdmit or bpedmit , X=Cl or Br) were determined by x-ray crystallography [10] .

The coordination mode of thioether-pyrazole ligands , 1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane(bdtp) and 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane(bddo) ligands in Pd(II) complexes containing a diphosphine ligand is determined by subtle changes in the size of the bridge between the two phosphorus atoms . The ^1H NMR and $^{31}P(^1H)$NMR at variable temperature prove that the hemilabile character of the bdtp ligand depend on the diphosphine ligand [11].

Three new nickel complexes have been synthesized with the ligand Hbss (4-mercapto-2-thia-1-butylbenzene) and Hbsms (2-benzylsulfonyl-2-methyl-5-propanethiol) . The complex $[Ni(bss)_2]$ is mononuclear with an S_4 coordination environment . The complexes $[Ni_3(bss)_4](BF_4)_2$ and $[Ni_3(bsms)_4](BF_4)_2$ are linear trinuclear complexes that can synthesized either directly from the ligands Hbss and Hbsms in a reaction with $[Ni(BF_4)_2]$. Crystals suitable for x-ray diffraction were obtained for $[Ni_3(bss)_4](BF_4)_2$ and the structure was determined by single crystal X-ray, which indicate that the nickel centers are a square planar environment [12] .

As a part of a chelating system thioether group are known to coordinate to metal ions [13,14] , and in view of these interesting results and as continnation to our studies on transition metal complexes with sulfur containing ligands [15-17] , we have prepared here a new ligands (L^1-L^4) and their dinuclear complexes with Ni(II) , Pd(II) and Pt(II) ions .

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2. Experimental

2.1 Materials

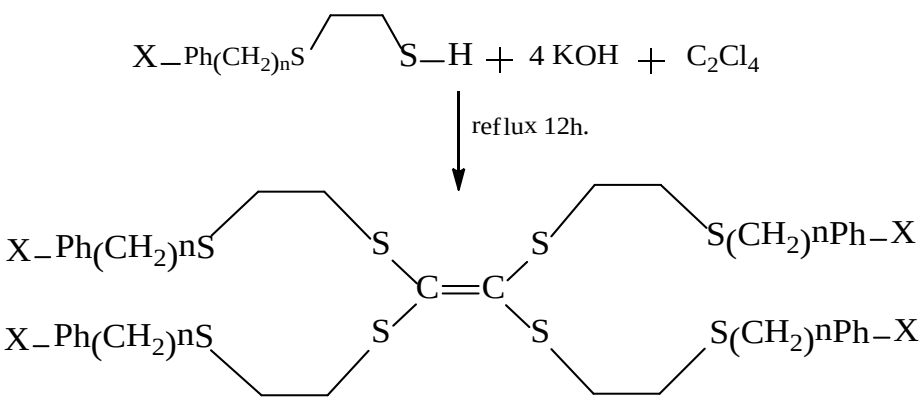
All preparation were carried out in reagent grade solvents . All chemicals used in the synthesis were obtained from Aldrich , Fluka or B.D.H and were used without further purification .

2.2 Preparation of the ligands

The starting materials were prepared according to the literature method[13].

Preparation of 1,1,2,2-tetrakis[2-(benzylthio)ethylthio]ethylene (L^1):

To a solution of 4-mercapto-2-thia-1-butyl benzene (0.73g , 0.004 mol) in 20 ml toluene was added to a solution of (0.23g , 0.004 mol) of KOH in ethanol 10 ml, then the mixture was added to a solution of tetrachloroethylene (0.17 g , 0.001 mol) in 10 ml ethanol . The mixture was stirred under reflux for 12h. on cooling the precipitate was obtained which was filtered off , washed several times with ethanol to remove the formed KCl , then it was washed with diethylether and then dried under vacuum for 4h . The preparation of the other ligands L^2-L^4 using similar procedure as shown in Scheme (1)



n = 1, X = H L^1
n = 0, X = o-CH_3 L^2
n = 0, X = P-Cl L^3
n = 0, X = o-NH_2 L^4

Scheme (1) : Preparation of the ligand

2.3 Preparation of the complexes :

2.3.1 Preparation of $[Ni_2(L)Cl_4]$ or $[Ni_2(L)Cl_2]Cl_2$ complexes :

A solution of $NiCl_2.6H_2O$ (0.47g , 0.002 mol) in (10 ml) ethanol was added to a stirred solution of the ligand (0.001 mol)in (10 ml) tetrahydro furan (THF). The mixture was refluxed for 2h . The mixture was left 12h. at room temperature to give the precipitate , which was filtered off several times with ethanol and diethylethe then dried under vacuum for several hours .

2.3.2 Preparation of $[Pd_2LCl_4]$: ($L=L^1-L^4$) :

The salt Na_2PdCl_4 was prepared by heating (0.35 g , 0.002 mol) of $PdCl_2$ and (0.23 g , 0.004 mol) of NaCl in 5 ml distilled water and added gradually with continuous stirring to (0.76 g , 0.001 mol) of ligand (L^1) in 20 ml of tetrahydrofuran . The mixture was refluxed for 2h , the solvent was evaporated in vacuum . Red brown powder was obtained , it was washed several times with distilled water and diethylether , the precipitate was dried under vacuum . The other complexes were prepared similarly .

2.3.3 Preparation of $[Pt_2LCl_4]$: ($L=L^1-L^4$) :

To a solution of L^1 (1,1,2,2-tetrakis[2-(benzylthio)ethylthio]ethylene) (0.76 g , 0.001 mol) in 20 ml tetrahydrofuran was added a solution of K_2PtCl_4 (0.83 g , 0.002 mol) in a 5 ml distilled water . The mixture was refluxed for 2h , the solvent was evaporated in vacuum to half volume , golden precipitate was obtained which washed several times with distilled water and diethylether , the precipitate was dried under vacuum for several hours .The other complexes were prepared similarly .

2.4 Physical measurements

Elemental analysis of the isolated complexes were accomplished by using (elementar vario micro cube) at Department of Chemistry , Liverpool University (U.K.). Metal content estimation were done on Sens AA GBC SCIENTIFIC EQUIPMENT 3000 Atomic absorption spectrophotometer at Mosul University , College of Basic Education. Conductivity measurements for 10^{-3} M solution of the complexes in (DMF) were carried out on Jenway 4510 conductivity meter at Mosul University , College of Science .The infrared spectra for ligands and complexes were recorded on a FT-IR (Brucker Alpha Sample Compartment RT-DlaTGS at the range (200-4000 cm^{-1}) without using KBr or CsI .This measurements were carried out at

Department of Chemistry , Liverpool University . The UV/Vis spectra were recorded on a Shimadzu UV-160 spectrophotometer for 10^{-3} M solution of the complexes in DMF using 1 cm quartz cell . Magnetic susceptibililties values were corrected for diamagnetic contribution using Pascal's constants and measured at 25°C on the solid state using Bruker B.M.6 instruments .

3. Results and discussion

The multidentate ligands (L^1-L^4) , not previously reported in the literature were prepared according to the following scheme (1) , by treatment of 4-mercapto-2-thia-1-butyl benzene or 2-methyl-4-mercapto-1-thia-1-butylb-enzene or 4-chloro-4-mercapto-1-thia-1-butylbenzene or 2-amino-4-mercapto-1-thia-1-butylbenzene ,with potassium hydroxide and tetrachl-oroethylene , yielded the desired products . The ligands were characterized by elemental analysis , IR , ^{1}H , ^{13}C NMR spectroscopy and electronic spectra . The IR and NMR data are in accordance with the proposed structures . Disappearance of the SH stretching vibration , related to the thiol functional group along with the growing of strong bond in the region 829-857 cm^{-1} due to the C-S bands , indicates the formation of the ligands , as well as the removal of the chloride ions confirmed by sodium fusion test and elemental analysis.

The ligands (L^1-L^4) are white to brown in color , are isolated in good yield and are pure by NMR and elemental analysis (Table 1) .

3.1 ^{1}H , ^{13}C NMR Spectra :

the ^{1}H , ^{13}C – NMR spectra of these ligands are first order at the field strength employed and peak assignment were straight forward . The ^{1}H NMR spectrum of (L^1) exhibit the aromatic protons were observed in the region 7.249 - 7.343 (m , 20 H) , 3.945 (t , H) , 3.946 – 3.879 (m , 8H , CH_2) , 3.819 (t , 1H) , 3.725 (s, 1H) , 3.146 (m , 3H) , 2.88 – 2.827 (m , 3H) , 2.693 – 2.646 (m , 5H) , 2.572 (d , 2H) for L^1 , and 6.840 – 7.411 (m , 16H , Ar) , 4.452 (S , 8H , NH_2) , 3.134 (m , 8H , CH_2) ; 2.898 (m , 8H , CH_2) for L^4 , the ^{13}C – NMR spectrum shows peaks at 30.4-35.33 ppm for (a – c) CH_2 , 127.5 for c = c and 128.9 – 139.0 ppm for aromatic carbon for L^1 , and 22 . 0 – 38.2 for (a – c) CH_2 and 125.5 for (C = C) and 128.47 – 148.0 ppm for aromatic carbon for L^4 as in fig (1) .

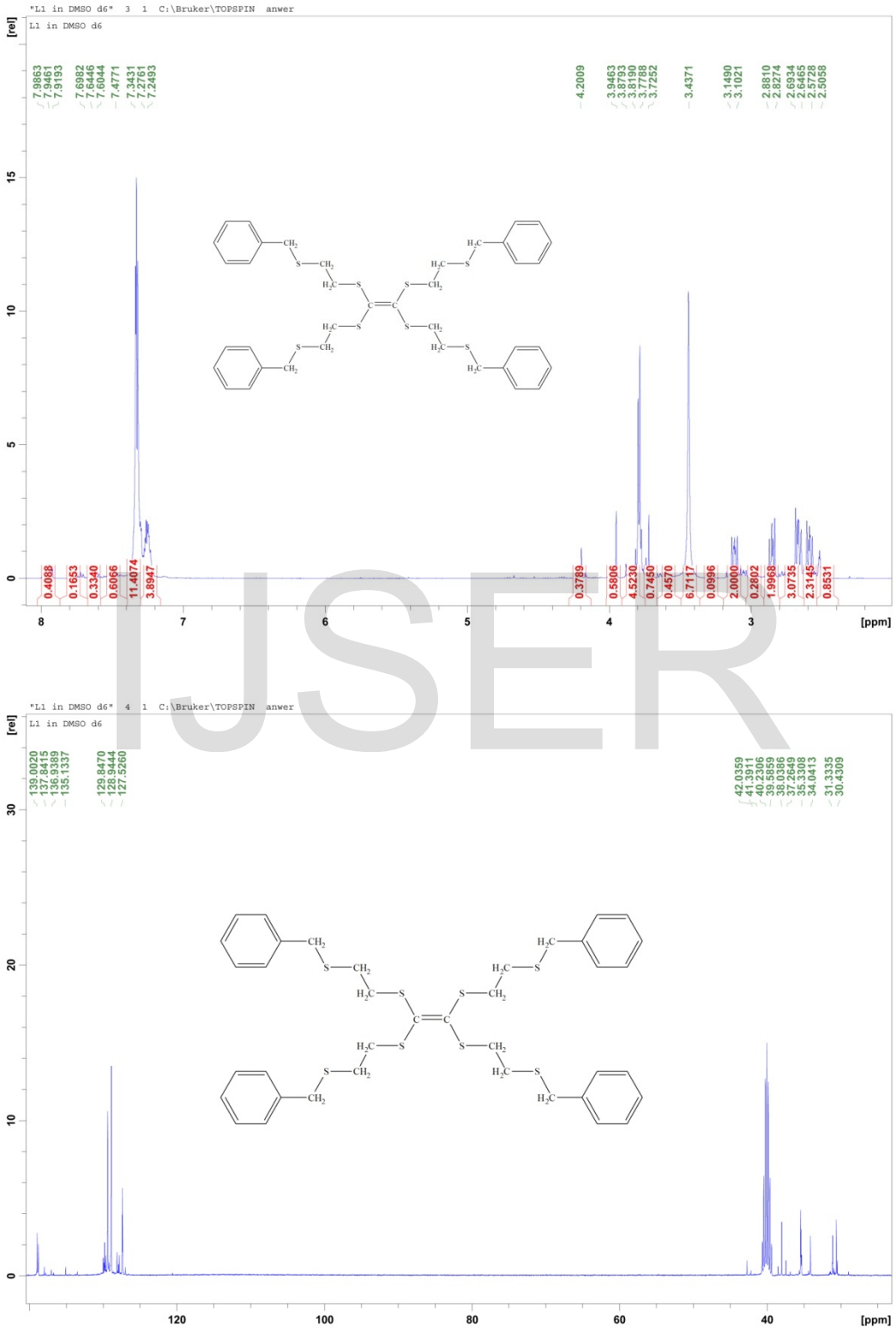
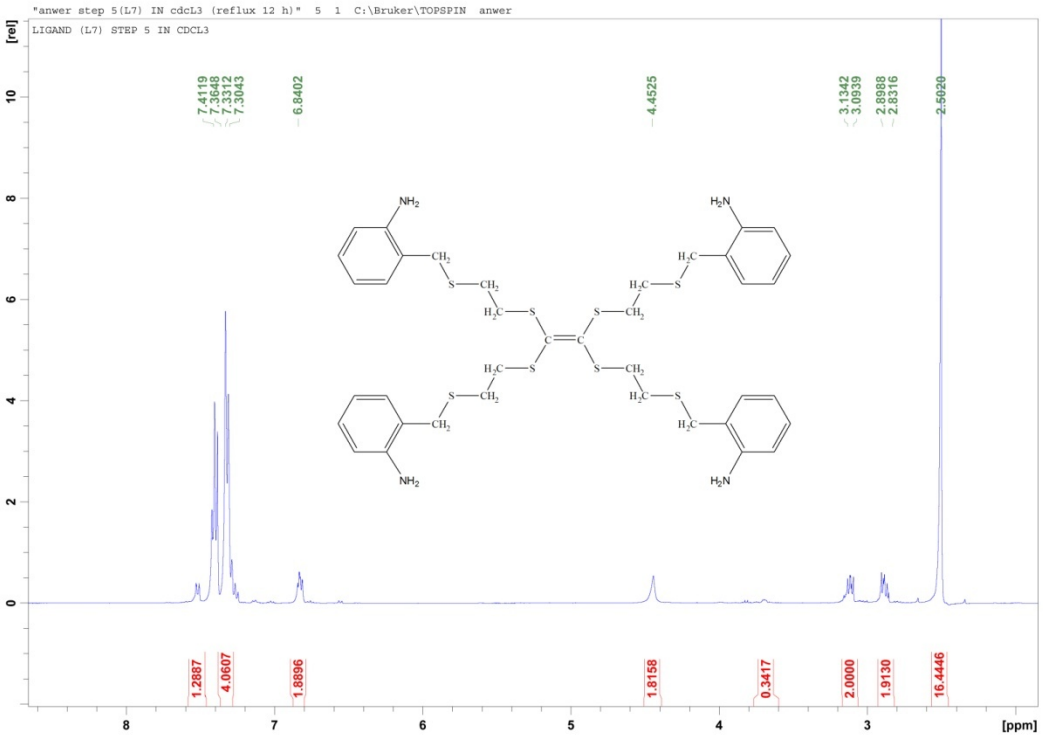


Fig 1a: ^{1}H, ^{13}C, for ligand (L^{1})



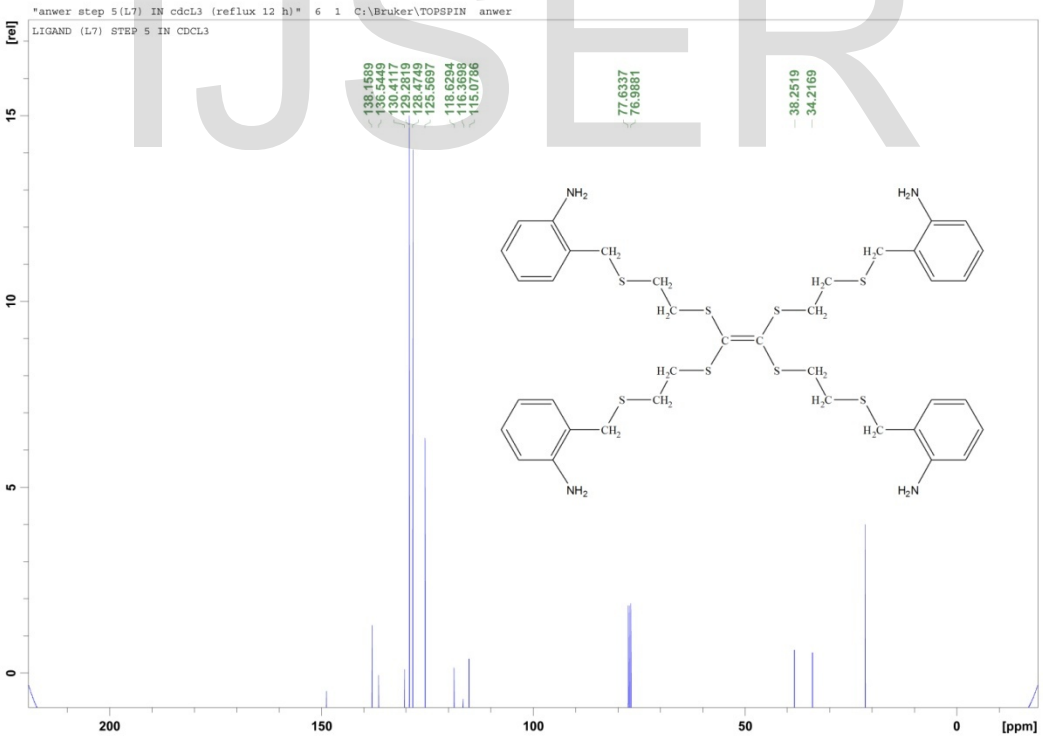


Fig. 1b : $^{1}H,^{13}C$ for ligand(L^{4}) .

The reaction of these ligands (L^1-L^4) with nickel(II) , palladium(II) and platinum(II) chloride in a (1:2) ligand to metal molar ratio gives the complexes of the formulas $[M_2(L)Cl_4]$ and $[Ni_2(L)Cl_2]Cl_2$, M = Ni , Pd , Pt , L = L^1-L^4 . The elemental analysis are consistent with the proposal molecular formula that show the ratio of ligand to metal is (1:2) .

The physical properties of the solid complexes are listed in Table (2) . The complexes are quite stable in air , fairly stable to heat and melt or decompose at abouts 135 – 309 °C . They are insoluble in common organic solvents, however, soluble in dimethyl formamide (DMF) or dimethyl-sulfoxide (DMSO).The electrical molar conductance of the complexes in 10^{-3} M (DMF) solution within the range 16 – 55 $ohm^{-1}.cm^2\ mol^{-1}$, indicating the neutral nature of the complexes excepts for the complexes of the formula $[Ni_2(L)Cl_2]Cl_2$ which are (1:2) electrolyte in nature [18] . This is consistent with stoichiometry assumed for the complexes on the basis of analytical data.

3.2 Infra-red Spectra

The most important IR assignments of the ligands as well as their bonding sites Table (3) have been determined by a careful comparison of the spectra of the ligands with those of their complexes . The IR spectra of the ligands showed a medium band at (1618 – 1660) cm^{-1} assigned to ν(C = C) vibration and this band remained unchanged in the spectra of all complexes . The ν(C - S) absorption band appeared at (829-857) cm^{-1} in the free ligands was found to appear at lower frequency in the spectra of all the complexes except in complexes (4,8,12) the shift of ν (C - S) is upward by (841-848 cm^{-1}) indicating the involvement of sulphur atoms of the ligands in the coordination with the metal ion [19]. The IR spectra of the ligand L^4 exhibited a band at the 3343 cm^{-1} region attributed to ν (NH_2) and this band remained almost constant upon coordination of this ligand with the metal ions. This indicates that the NH_2 group had not participated in the coordination .

Moreover , the IR spectra of the complexes showed new bands at 350-375 cm^{-1} which tentatively assigned to ν (M – S) respectively (M = Ni , Pd , Pt) [20]. Further , the IR spectra of the complexes showed another new band in the region of 295 – 325 cm^{-1} which may well be due to ν (M – Cl) frequency [21] . This band split into two bands and this can be taken as evidence for square planar cis configuration of these complexes (M = Pd or Pt) . The effective magnetic moment values of the complexes and presented in Table (2) .The Ni(II) complexes has a μ_{eff} value of 3.15 – 3.65 B.M which suggest a tetrahedral geometry , while all Pd(II) and Pt(II) are diamagnetic as expected for d^8-metal ion in a square plane field[22] .

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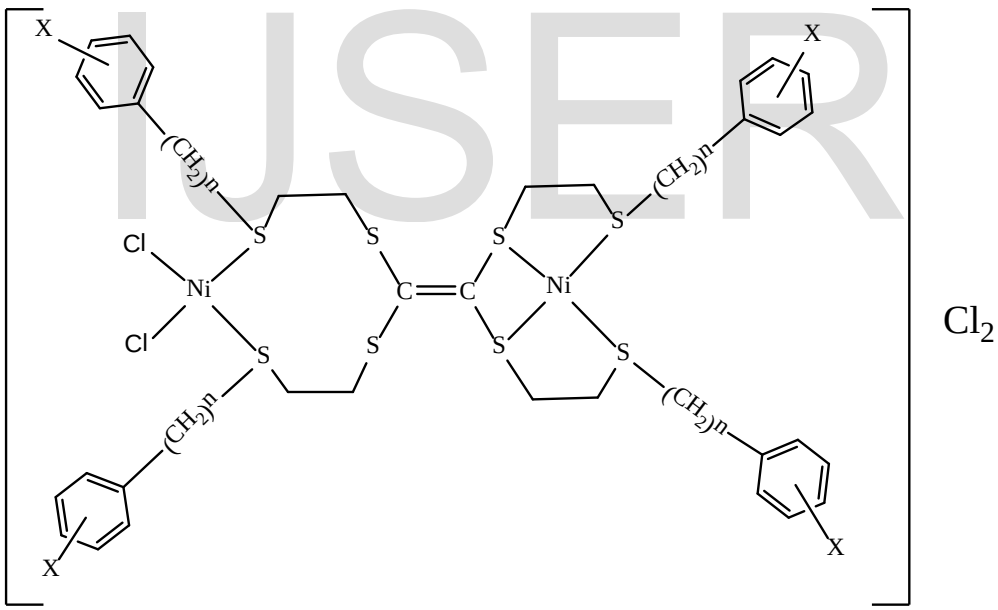
3.3 Electronic Spectra :

In order to obtain some more information about the coordination behaviors of the metal ions, the electronic spectra of the complexes have been recorded . The tentative assignments of the absorption bands from the electronic spectra of the ligands and their complexes and listed in Table (3) . Then π^*transition associated with the ligands were found in the region cm^{-1}. The Ni(II) complexes exhibits bands at (12919 – 14492 cm^{-1}) indicating the transition $^3T_1(F) \longrightarrow {}^3T_1(P)(\nu_3)$ in a tetrahedral geometry [23]. The (d – d) bands for the spectrum of the complexes of Pd(II) and Pt(II) having low intensities appeared at (22727-25641 cm^{-1}) were assigned to the $^1A_1g \longrightarrow {}^1A_2g$ transition , in square planer environment around Pd(II) and Pt(II) with D_4h symmetry [24] .

On the basis of the foregoing results , the ligand used is this study , coordinate to the metal ions in tetrahedral and square planner fashion from the S sites of the ligand forming the dinclear complexes as shown in fig. (2).



Complex no. (1,2)

Fig 2a: Suggested structure for nickel complexes

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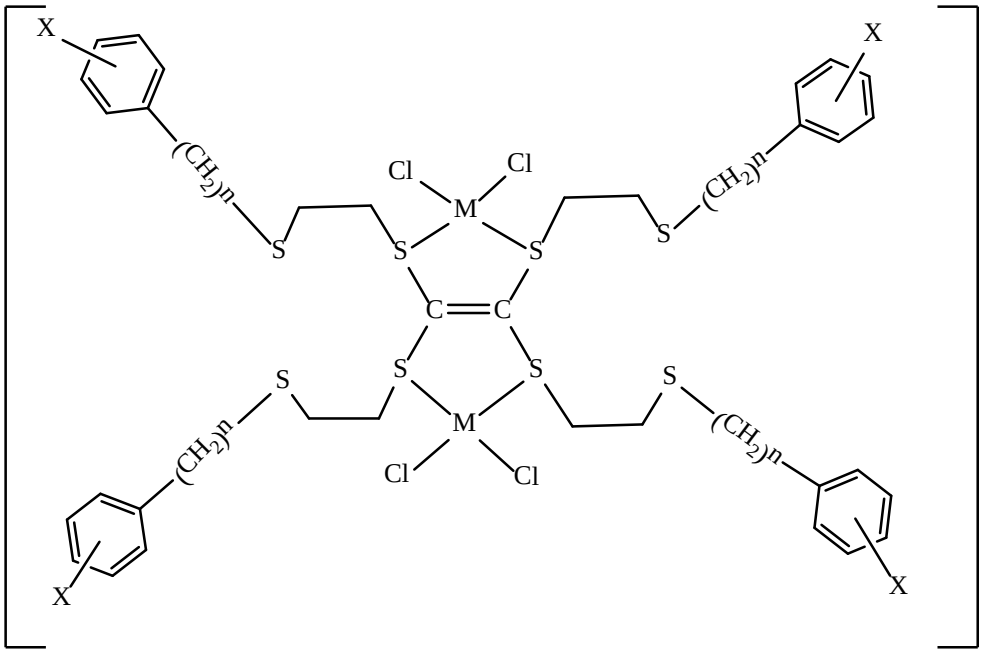

M = Ni , Pd or Pt , n=0,1

Fig. 2b : Suggested structures for the complexes

Table (1) : Some physical properties and elemental analysis of the prepared ligands .

Ligand Seq.	Chemical formula	M . p (°C)	Color	Yield	Analysis found / (calc.)			
					C%	H%	N%	S%
L^1	$C_{38}H_{44}S_8$	231-233	Beige	65	59.71 (60.31)	5.42 (5.82)	----	33.64 (33.86)
L^2	$C_{38}H_{44}S_8$	285-288	Pale yellow	67	60.20 (60.31)	5.61 (5.82)	----	32.90 (33.86)
L^3	$C_{34}H_{32}S_8Cl_4$	255-258	White	63	48.46 (48.68)	3.64 (3.81)	----	30.23 (30.54)
L^4	$C_{34}H_{40}N_4S_8$	130 d	Light brown	72	53.99 (53.68)	5.51 (5.26)	7.86 (7.36)	32.74 (33.68)

d= decomposition

Table (2) : Analytical data and physical properties of the complexes .

No.	Complexes	M. p. (°C)	Colour	Yield	Analysis found / (calc.)						μ_{eff} B.M
					C%	H%	N%	S%	M%	Λ_M $Ohm^{-1}.cm^2.mol^{-1}$	
1	$[Ni_2L^1Cl_2]Cl_2$	156 d	Brown	96	44.30 (44.51)	4.15 (4.29)	----	24.76 (24.98)	11.18 (11.56)	138	3.65
2	$[Ni_2L^2Cl_2]Cl_2$	218 d	Light brown	51	44.75 (44.90)	4.26 (4.33)	----	24.87 (25.21)	11.00 (11.56)	121	3.15
3	$[Ni_2L^3Cl_2]$	150 - 152	Light brown	50	42.35 (42.70)	3.22 (3.34)	----	25.92 (26.79)	9.59 (10.70)	14	3.53
4	$[Ni_2L^4Cl_4].2H_2O$	307 - 309	Light brown	65	38.67 (40.02)	4.17 (3.92)	5.30 (5.49)	24.26 (25.11)	11.65 (11.52)	29	3.58
5	$[Pd_2L^1Cl_4]$	140-142	Brown	94	40.06 (41.05)	3.67 (3.96)	----	22.18 (23.04)	18.21 (19.15)	20	Dia
6	$[Pd_2L^2Cl_4]$	182 d	Dark brown	60	40.76 (41.05)	3.81 (3.96)	----	22.91 (23.04)	17.70 (19.10)	55	Dia
7	$[Pd_2L^3Cl_4]$	200 d	Dark brown	95	33.91 (34.20)	2.77 (2.68)	----	21.61 (21.46)	16.12 (17.84)	22	Dia
8	$[Pd_2L^4Cl_4]$	260 d	Dark brown	68	36.01 (36.62)	3.70 (3.59)	4.49 (5.02)	22.59 (22.98)	18.71 (19.08)	50	Dia
9	$[Pt_2L^1Cl_4].2H_2O$	135 d	Orange	78	34.43 (35.39)	3.32 (3.41)	----	19.33 (19.87)	----[a]	10	Dia
10	$[Pt_2L^2Cl_4]$	117 - 119	Black	72	35.23 (35.39)	3.53 (3.41)	----	19.48 (19.87)	----[a]	39	Dia
11	$[Pt_2L^3Cl_4]$	170 - 172	Brown	63	28.92 (29.77)	2.43 (2.33)	----	18.79 (18.68)	----[a]	71	Dia
12	$[Pt_2L^4Cl_4]$	142-145	Olive green	62	32.01 (31.57)	3.61 (3.09)	4.37 (4.33)	20.20 (19.81)	----[a]	41	Dia

d= decomposition , a= platinum cathode is not available

Table (3) : Infrared , electronic spectra of the free ligands and their metal complexes

Compound seq.	ν (C=C)	ν (C-S)	ν (M-S)	ν (NH_2)	ν (M-Cl)	U.V./Visible Band maxima λ_{max} (cm^{-1})
L^1	1653(m)	857(m)	----	----	----	34246,37593
L^2	1647(m)	839(m)	----	----	----	35211
L^3	1655(m)	849(m)	----	----	----	35714,40983
L^4	1618(s)	829(w)	----	3343(b)	----	32467
1	1662(m)	829(m)	362(w)	----	305(w) 325(w)	12919, 32679
2	1655(m)	829(m)	365(w)	----	300(m) 326(m)	14450
3	1655(m)	831(m)	352(w)	----	297(m) 315(w)	14492,28571
4	1620(m)	877(w)	360(w)	3327(b)	294(w) 320(m)	14409 ,33333
5	1662(w)	822(w)	370(w)	----	295(m) 325(m)	24630
6	1653(m)	822(s)	352(w)	----	305(m) 325(m)	22727
7	1662(m)	820(w)	350(w)	----	295(m) 322(w)	24038
8	1624(m)	872(w)	350(w)	3347(b)	297(w) 315(m)	23980
9	1661(m)	835(w)	355(w)	----	300(m) 325(w)	24038
10	1653(m)	830(w)	375(w)	----	290(w) 315(w)	23474
11	1653(m)	835(w)	360(w)	----	280(w) 305(w)	25000
12	1613(w)	870(w)	370(w)	3339(b)	297(w) 310(w)	25641

4. Conclusion :

The results of this study clearly indicated that the sulfur rich ethylene ligands are coordinate to Pd^{2+} and Pt^{2+} as tetradentate fashion while for Ni^{2+} are tetradentate and hexadentate fashion from sulfur atoms of the ligands and the chloride ions of the metal ions .

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