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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 (L1-L4), 1,1,2,2-tetrakis [2-(benzylthio)ethylthio]ethylene(L1),1,1,2,2-tetrakis [2-(o-tolylthio) ethylthio]) ethylene (L2) , 1,1,2,2-tetrakis [3-(p-chlorophenylthio) ethylthio] ethylene (L3) and 1,1,2,2-tetrakis [2-(o-aminophenylthio) ethylthio] ethyene (L4) 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 : [M2(L)Cl4] and [Ni2(L)Cl2]Cl2 M=Ni(II) , Pd(II) and Pt(II) , L=L1-L4 . The synthesized ligands have been characterized on the basis of their elemental analysis , FTIR, 1H ,13C 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), Pt(II) complexes, Square planar complexes

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 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

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diphosphine ligand is determined by subtle changes in the size of the bridge between the two phosphorus atoms . The ^{1}H NMR and $^{31}P(^{1}H)$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 .

Experimental

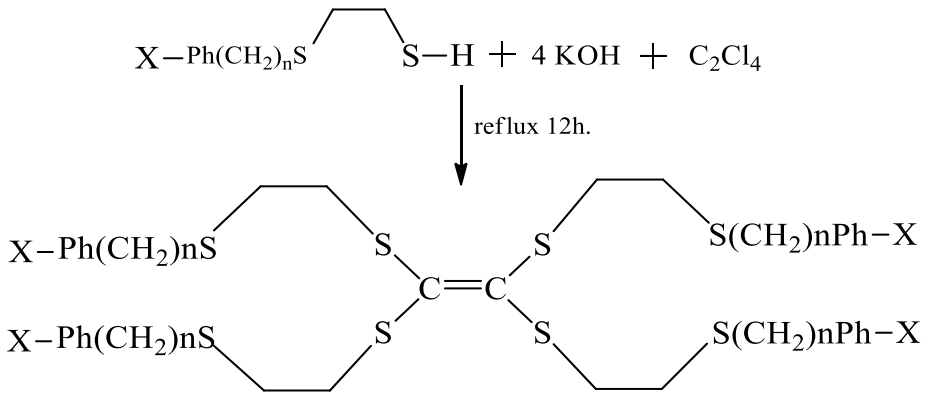
All preparation were carried out in reagent grade solvents. All chemicals used in the synthesis were obtained from Aldrich, Fluka or B.D.H and were used without further purification.

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 (L1):

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 L2-L4 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

Preparation of [Ni2(L)Cl4] or [Ni2(L)Cl2]Cl2 complexes :

A solution of NiCl2.6H2O (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 .

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 .

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.

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.

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, ^1H, ^{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) . the ^1H , ^{13}C – NMR spectra of these ligands are first order at the field strength employed and peak assignment were straight forward . The ^1H 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) .

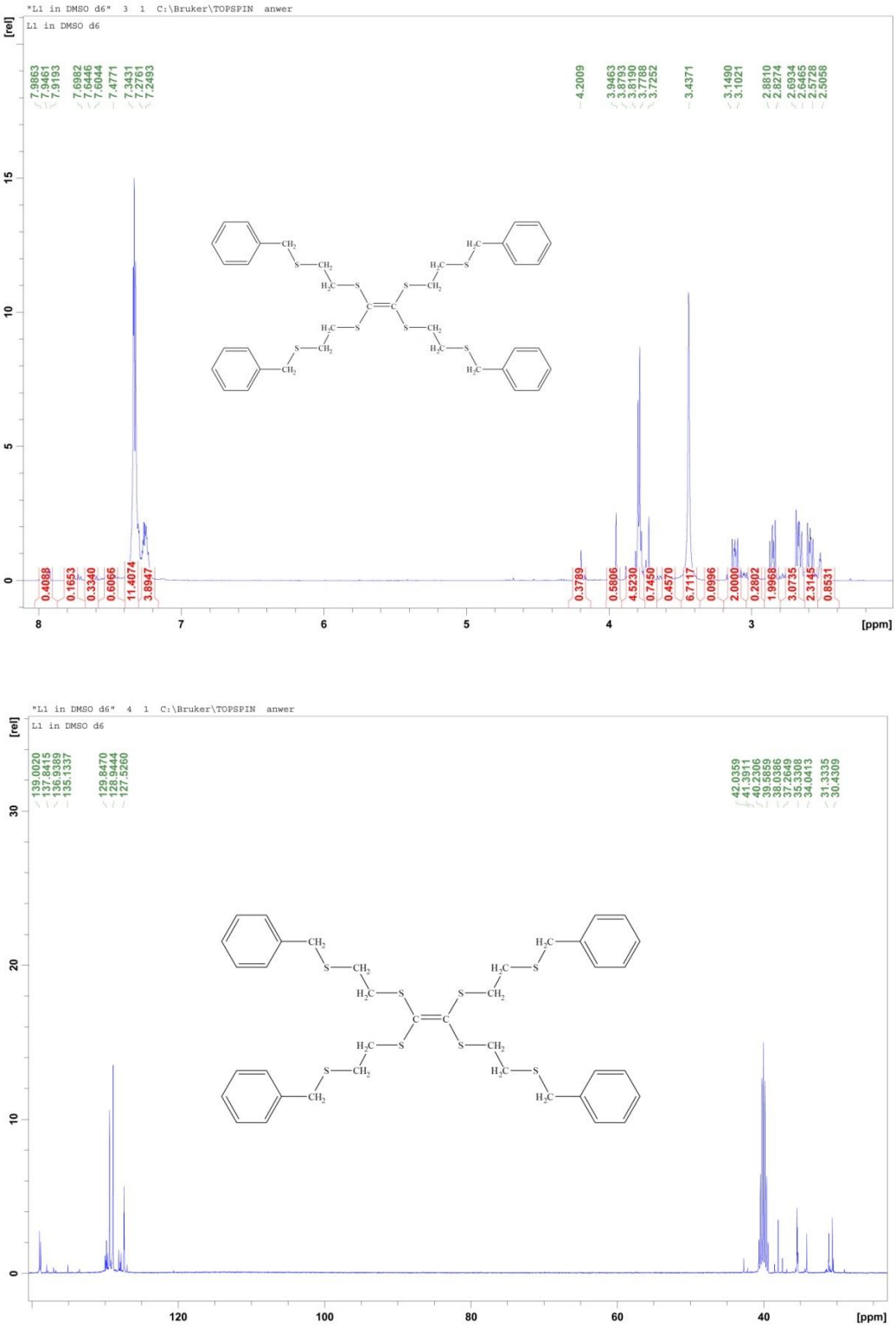


Fig 1a. 1H, 13C, for ligand (L1)

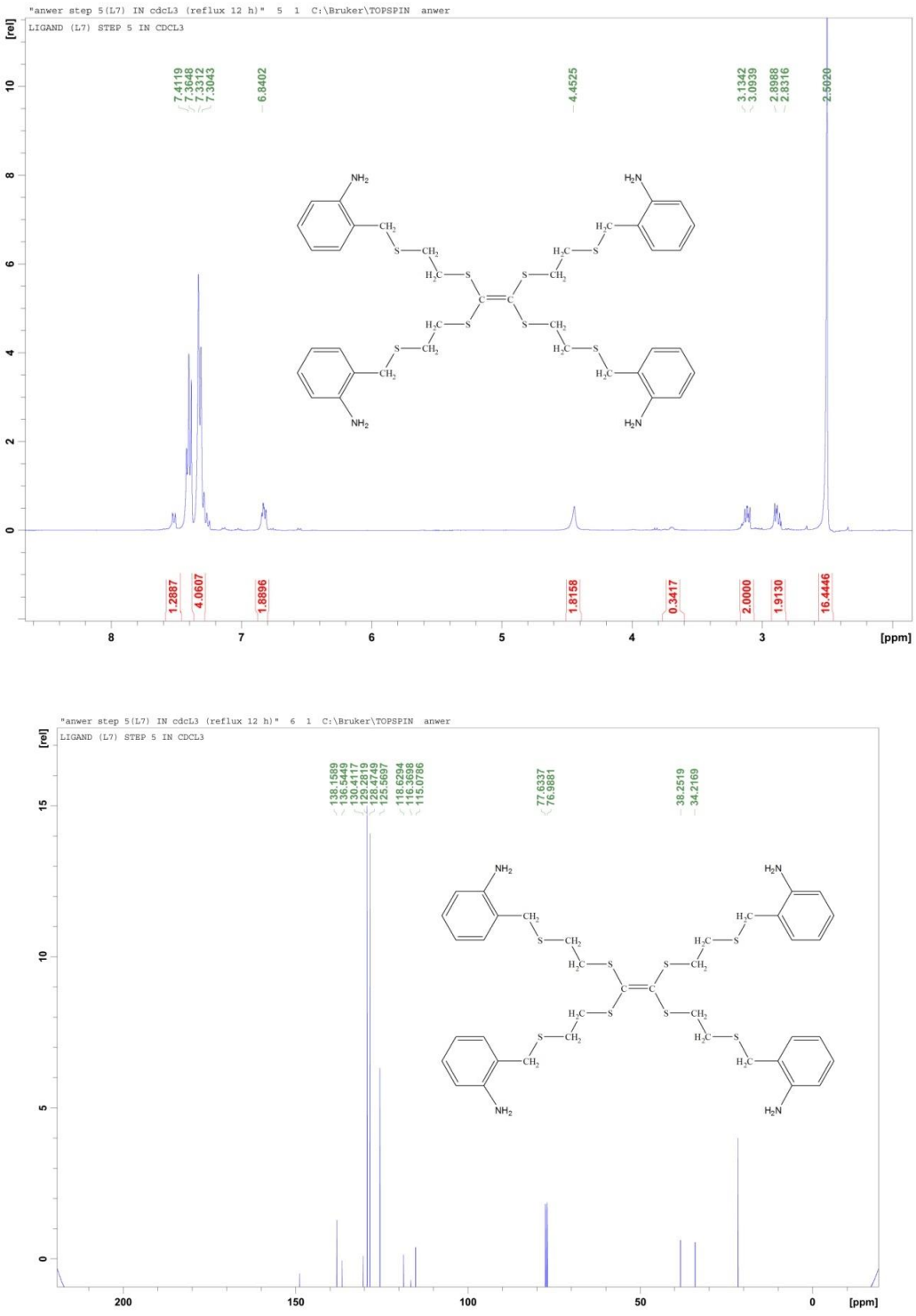


Fig. 1b. 1H,13C for ligand(L4)

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

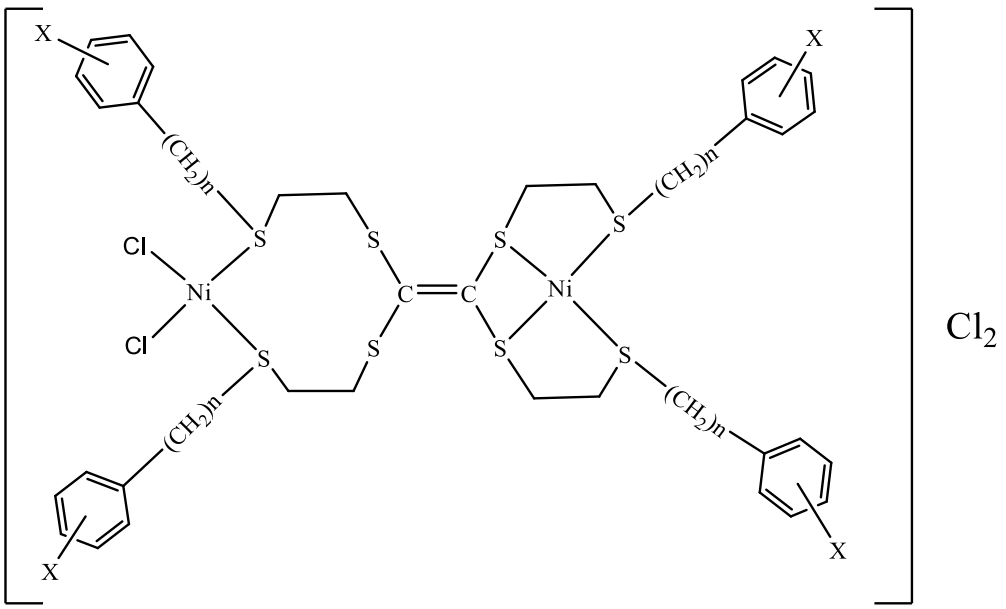
conductance of the complexesin 10^{-3} M (DMF) solution within the range 16 – 55 $ohm^{-1}.cm^2$ mol^{-1}, indicating the neutral nature of the complexes excepts for the complexes of the formula $[Ni_2(L)Cl_2]Cl_2$ which are (1:2) electrolyte in nature [18] . This is consistent with stoichiometry assumed for the complexes on the basis of analytical data.

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.

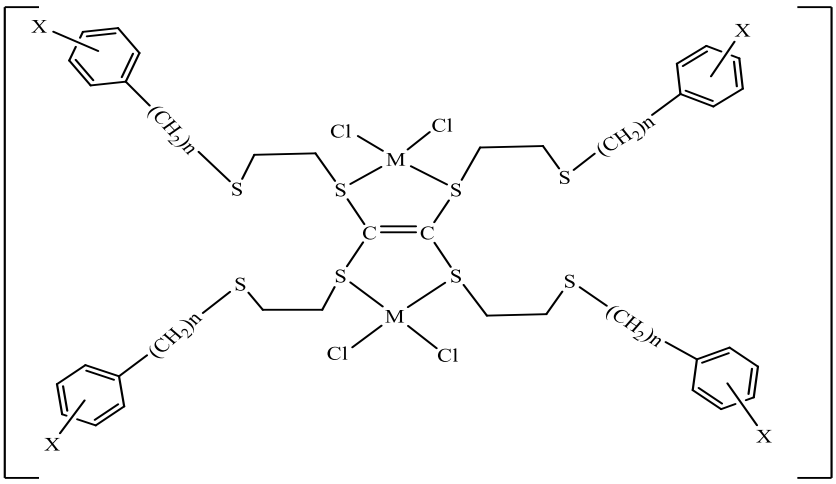
Moreover, the IR spectra of the complexes showed new bands at 350-375 cm^{-1} which tentatively assigned to ν (M – S) respectively (M = Ni, Pd , Pt) [20]. Further, the IR spectra of the complexes showed another new band in the region of 295 – 325 cm^{-1} which may well be due to ν (M – Cl) frequency [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] .

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 (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



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.)					Λ_M, $Ohm^{-1}.cm^2.mol^{-1}$	μ_{eff} B.M
					C%	H%	N%	S%	M%		
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

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