



## Synthesis and Characterization of Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> Complexes with Benzimidazole-2-thionate, Diphosphene and Their Reaction with Iodine

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Nickel, copper or zinc metal react with *bis*-benzimidazole disulfide (C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>S<sub>2</sub>) (L1) in refluxing ethanol-toluene to give the complexes of the type [M(L)<sub>2</sub>], where M = Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and L = benzimidazole-2-thionate (C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>S<sup>-</sup>) through an oxidative addition reaction. The complexes of type [M(L)<sub>2</sub>Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>], n = 1, 2 or 3, were prepared by direct reaction of [M(L)<sub>2</sub>] with diphosphene ligand in (1:1) and (2:2) molar ratio respectively. The reaction of some of the above complexes with iodine was also carried out. The complexes were characterized by microanalysis, IR, UV-visible spectroscopy, molar conductivity and magnetic moment and solid state electrical conductivity measurements. Electronic and magnetic measurements indicate that some of the complexes have square planar geometry and the other contain tetrahedral and octahedral geometries. Solid state electrical conductivity of compact pellets suggest that the complexes are non conducting while with the iodinated complexes behave as typical semiconductors as their conductivities were found to increase with temperature.

**Key Words:** Synthesis, Characterization, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Complexes, Benzimidazole-2-thionate.

### INTRODUCTION

There has been considerable interest in the study of organic ligands containing two or more different donor atoms because such ligands through light on the nature of the metal-ligands bonding.

Selenium and bismuth metals react with di-2-pyridyl-disulfide (Py<sub>2</sub>S<sub>2</sub>) in refluxing toluene to give the compounds Se(pyS)<sub>4</sub> and Bi(pyS)<sub>3</sub> in high yield. Reactions of selenium or bismuth/Py<sub>2</sub>S<sub>2</sub> and iodine in different molar ratio was carried out in refluxing toluene led to the formation of Se(pyS)<sub>3</sub>I, Se(pyS)<sub>2</sub>I<sub>2</sub>, Bi(pyS)<sub>2</sub>I and Bi(pyS)I<sub>2</sub> respectively. All the compounds were characterized physico-chemically and their antibacterial activity were studied<sup>1,2</sup>.

Copper and nickel powder react directly with sodium dithiocarbamate in organic solvents and produce the corresponding metal complexes. The result showed that the copper powder react in chloroform more readily than any other system examined. This reaction has been successfully applied in the determination of copper content in brass and bronze powder<sup>3</sup>.

The powder of tin metal is oxidized by Et<sub>2</sub>P(S)SS(S)PEt<sub>2</sub> to tin(II) diethyldithiophosphate, the reaction involve the insertion of the metal into the S-S bond<sup>4</sup>.

The reactions between [(COD)PtCl<sub>2</sub>], COD = 1,5-cyclo octadiene and the tin thiolate compounds (Ph)<sub>3</sub>Sn(SPh) and (Ph)<sub>2</sub>Sn(SPh)<sub>2</sub> have been studied. The formal reaction yield two new Pt-Sn heterobimetallic complexes depending on the molar ratios of [(COD)PtCl<sub>2</sub>]/PhSn(SPh). For a 1:2 molar ratio the complex (COD)Pt(SPh)<sub>2</sub>(Cl)Sn(Ph)<sub>3</sub>·2CH<sub>2</sub>Cl<sub>2</sub> was obtained. For a 1:1 molar ratio the complex formed was (COD)Pt(SPh)(Cl)<sub>2</sub>Sn(Ph)<sub>3</sub>·3CH<sub>2</sub>Cl<sub>2</sub> through an oxidative addition reaction. The complexes were characterized by IR, <sup>1</sup>H, <sup>13</sup>C NMR, <sup>195</sup>Pt-NMR, <sup>119</sup>Sn-NMR and Mössbauer spectroscopies<sup>5</sup>.

Tetramethylthiuram disulfide (TDS) an inhibitor or rephrotoxicity of Pt(II) drugs, an efficient agent in the treatment of chronic alcoholism and heavy metal toxicity. The reactions of tetramethylthiuram disulfide with K<sub>2</sub>PtCl<sub>4</sub> in 1:1 or 1:2 molar ratio gave the compounds [PtCl<sub>2</sub>(TDS)] and [Pt(S<sub>2</sub>(NET<sub>2</sub>)<sub>2</sub>)] respectively, were described by Cerrantas *et al.*<sup>6</sup>.

Indium reacts with (C<sub>3</sub>H<sub>4</sub>N<sub>3</sub>S)<sub>2</sub> or (C<sub>5</sub>H<sub>14</sub>N<sub>3</sub>S<sub>2</sub>) in refluxing toluene give the compounds [In(L1)<sub>3</sub>] and [In(L2)<sub>3</sub>], L1 = C<sub>3</sub>H<sub>4</sub>N<sub>3</sub>S<sup>-</sup>, L2 = C<sub>5</sub>H<sub>14</sub>N<sub>3</sub>S<sup>-</sup> through an oxidative addition reaction. Trinuclear complexes of the formula [In(L1)<sub>3</sub>(MCl<sub>2</sub>)<sub>2</sub>] and [In(L2)<sub>3</sub>(MCl<sub>2</sub>)<sub>2</sub>] were prepared by direct reaction of

$MCl_2 \cdot 6H_2O$  ( $M = Co, Ni$ ) or  $CuCl_2 \cdot 2H_2O$  and  $ZnCl_2 \cdot XH_2O$  with the above indium complexes. The prepared compounds and complexes were characterized by micro analysis, IR, UV-visible spectra, metal content, conductivity and magnetic measurements<sup>7</sup>.

Palladium(II) and platinum(II) complexes containing the mixed ligands  $Ph_2P(CH_2)_nPPH_2$ ,  $n = 1-4$  and benzo-1,3-imidazoline-2-thione, benz-1,3-oxazoline-2-thione or benzo-1,3-thiazoline-2-thione have been prepared and characterized by elemental analysis, spectral and magnetic studies as well as  $^{31}P$ ,  $^1H$  NMR data<sup>8</sup>.

Homo binuclear complexes of the type  $[Cl_2MRC=CRMCl_2]$  [ $M = Ni(II), Pd(II)$  or  $Pt(II)$  and  $R = 5$ -phenyl-1,3,4-oxadiazole-2-thiol, 4,5-diphenyl-1,2,4-triazole-3-thiol, or 2-mercapto-benzothiozole] have been prepared and characterized. Octahedral environment around  $Ni(II)$ , while square planar geometry around  $Pd(II)$  or  $Pt(II)$  have been deduced on the basis on the magnetic and spectral measurements<sup>9</sup>.

Metal dithiolene complexes possess a delocalized electron system as a planar central core  $[M(C_2S_2)_2]$ . The conduction band is formed by the ligand p or orbital or mixed-metal-ligand orbital where the sulfur atoms play an important role<sup>10</sup>.

Milsubayashi *et al.*<sup>11</sup> reviewed donor abilities of the diimredithiolene complexes. The complexes provide cation salts with various anions including  $I_3^-$  or  $Br_3^-$ .

In view of these interesting results and in continuation of our comprehensive studies on transition and non transition metals complexes with sulfur containing<sup>12,13</sup> and other various donor ligands<sup>14,15</sup>, we reported here the preparation of some  $Ni(II)$ ,  $Cu(II)$  and  $Zn(II)$  complexes with hybrid ligands of benzimidazole-2-thionate and diphosphine.

## EXPERIMENTAL

All the chemicals used were of high purity according to the supplier (Fluka). Analysis of ligand and complexes were carried out using CHNS elemental analyzer model 2400 Perkin Elmer. The metal content was estimated spectrophotometrically using Shimadzu AA670 spectrophotometer. Melting point or decomposition temperature were determined on a Buchi melting point apparatus and were uncorrected, infrared spectra were recorded on a FTIR Bruker Tensor 27 Co. spectrophotometer in the  $4000-250\text{ cm}^{-1}$  range using CsI disc. Electronic spectra were obtained with a Shimadzu UV-visible recording UV1600 spectrophotometer at room temperature; these measurements were recording using a concentration of  $10^{-3}\text{ M}$  of the complexes in DMSO. The magnetic moments were carried out at  $25\text{ }^\circ\text{C}$  on the solid state by Faradays method using Bruker BM6 instruments, conductivities were measured using conductivity meter model PCM3- Jenway. These measurements were obtaining using DMSO over the  $10^{-3}\text{ M}$  solution at  $25\text{ }^\circ\text{C}$ .

The solid state electrical conductivities of compact samples were measured as a function of temperature (308-328 K), on a Hewlett-Pakard LCR meter by the conventional two probe method. The pellets were prepared at load of  $(5-7\text{ torr/cm}^3)$  and the contact on the pellet surface was made with the help of silver paste.

Benzimidazole disulfide was synthesized by a standard method<sup>16</sup>.

## Synthesis of the complexes

**Preparation the complexes 1-3 of the type  $[M(L)_2]$ ,  $M = Ni, Cu$  or  $Zn$  ions and  $L = (C_7H_5N_2S^-)$ :** A clear solution of benzimidazoledisulfide (0.3 g, 0.001 mol) in tetrahydrofuran (20 mL) was added to the metal powder ( $M = Ni, Cu$  or  $Zn$ ) (0.001 mol) in (30 mL) ethanol-toluene. The reaction mixture was stirred under reflux for 12 h, by which time the metal was completely dissolved, refluxing was stopped at this stage and the stirred mixture was cooled to ambient temperature. The formed precipitate was filtered off washed with ethanol and diethyl ether and dried under vacuum.

**Preparation the complexes 4-6 of the type  $[M(L)_2(Dppm)]$ , 9-11 of the type  $[M(L)_2(Dppe)]$  and 14-16  $[M(L)_2(Dppp)]$ ,  $M = Ni, Cu, Zn$  ions and  $Dppm = bis\text{-}(diphenylphosphino)\text{methane}$ ,  $Dppe = 1,2\text{-bis}\text{-}(diphenylphosphino)\text{ethane}$  and  $Dppp = 1,3\text{-bis}\text{-}(diphenylphosphino)\text{propane}$ :** A solution of  $[M(L)_2]$  complexes (0.001 mol) in (10 mL) toluene was added to a solution of (0.38 g, 0.001 mol) of  $Dppm$  in (5 mL) toluene, or (0.40 g, 0.001 mol) of  $Dppe$  in (5 mL) toluene, or (0.41 g, 0.001 mol) of  $Dppp$  in (5 mL) toluene. The reaction mixture was stirred under reflux for 4 h. The formed precipitate was filtered off, washed with toluene and diethyl ether then dried under vacuum for several hours.

The rest of the complexes were prepared using the above procedure.

**Preparation the complexes 7 and 12 of the type  $[Ni(L)_2(Dppm)]_2$  and 8 and 13 of the type  $[M(L)_2(Dppe)]_2$ ,  $M = Ni$  or  $Cu$  ions:** A solution of  $[M(L)_2]$  (0.002 mol) in (20 mL) ethanol-toluene was added to a solution of (0.77 g, 0.002 mol) of  $Dppm$  in (10 mL) ethanol-toluene or (0.79 g, 0.002 mol) of  $Dppe$  in (10 mL) ethanol-toluene. The mixture was stirred under reflux for 6 h. The mixture was left at room temperature for 12 h. A coloured precipitate formed in solution was filtered off, washed with ethanol and diethyl ether and then dried under vacuum for several hours.

**Preparation the complexes 17 and 18 of the type  $[M(L)_2]I$  complexes,  $M = Ni, Cu$  ions:** A solution of  $[M(L)_2]$  (1 mmol) in ethanol-toluene (20 mL) was added to iodine (0.25 g, 0.002 mol) in (20 mL) of toluene. The mixture was refluxed for 10 h with continuous stirring. The precipitate was obtained after evaporation of the residue solution to about 1/3 of its volume, which was filtered off, washed with ethanol and diethyl ether, then dried under vacuum.

**Preparation the complexes 19 and 20 of the type  $[M(L)_2Ph_2PCH_2PPh_2]I$ ,  $M = Ni$  or  $Cu$  ions:** The complexes of general formula  $[M(L)_2Ph_2PCH_2PPh_2]$  were prepared by mixing a solution of (1 mmol) of the complex  $[M(L)_2Ph_2PCH_2PPh_2]$  in (15 mL) of dimethylformamide with iodine (0.25 g, 0.001 mol) in toluene (15 mL).

Then the procedure was completed as above.

## RESULTS AND DISCUSSION

The complexes of the type  $[M(L)_2]$  were prepared through an oxidative addition reaction. These reactions are noticeably simpler than those used for the preparation  $[M(PhS)_n]$  compounds of main group elements involving the reaction of  $MCl_2$  with  $NaSPh$  or  $LiSPh$ <sup>17</sup>. The mechanism of oxidative addition reactions involving the initial cleavage of the S-S bond

TABLE-I  
PHYSICAL PROPERTIES OF THE PREPARED COMPLEXES

Comp.	Colour	m.p. (°C)	Elemental analysis (%): Found (calcd.)					$\Lambda$ ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	$\mu_{\text{eff}}$ (B.M)
			C	H	N	S	M		
L	White		56.32 (56.37)	3.31 (3.35)	18.75 (18.79)	21.93 (21.98)	-	10	-
1	Green	240	47.06 (47.09)	2.78 (2.80)	15.63 (15.70)	17.91 (17.94)	16.39 (16.45)	6.3	Dia
2	Brown	>350	46.42 (46.46)	2.74 (2.77)	15.43 (15.49)	17.69 (17.70)	17.54 (17.58)	11.4	2.20
3	Off white	228*	46.20 (46.24)	2.73 (2.75)	15.40 (15.41)	17.54 (17.61)	17.91 (17.98)	5.0	Dia
4	Dark olive	285*	66.00 (66.03)	4.50 (4.52)	7.87 (7.90)	9.00 (9.03)	8.25 (8.28)	4	0.03
5	Olive	260*	66.39 (66.42)	4.67 (4.70)	7.73 (7.75)	8.82 (8.85)	8.10 (8.12)	8	Dia
6	Dark green	250*	66.75 (66.78)	4.83 (4.88)	8.12 (8.14)	8.16 (8.69)	7.94 (7.97)	5.25	Dia
7	Olive	290*	63.24 (63.35)	4.30 (4.33)	7.52 (7.58)	8.61 (8.66)	7.92 (7.95)	8.5	Dia
8	Dark olive	305*	63.72 (63.77)	4.56 (4.51)	7.14 (7.44)	8.41 (8.56)	7.71 (7.77)	6.0	Dia
9	Dark brown	290*	65.55 (65.59)	4.47 (4.49)	7.81 (7.85)	8.95 (8.97)	8.80 (8.83)	4.9	2.08
10	Pale brown	255*	65.96 (65.99)	4.63 (4.67)	7.67 (7.69)	8.77 (8.79)	8.71 (8.73)	10	1.86
11	Pale brown	298*	66.31 (66.35)	4.82 (4.85)	7.52 (7.55)	8.60 (8.63)	8.50 (8.57)	6.0	2.04
12	Pale brown	265*	62.27 (62.29)	4.28 (4.30)	7.50 (7.53)	8.55 (8.60)	8.51 (8.54)	8.0	2.00
13	Pale brown	254	63.33 (63.36)	4.45 (4.48)	7.36 (7.39)	8.41 (8.45)	8.36 (8.39)	7.0	1.63
14	Pale green	348	65.39 (65.42)	4.43 (4.47)	7.80 (7.83)	8.91 (8.95)	9.33 (9.30)	6.0	Dia
15	Very pale brown	258	65.79 (65.81)	4.61 (4.66)	7.63 (7.67)	8.34 (8.77)	8.92 (8.96)	8.0	Dia
16	Greenish	344	66.13 (66.19)	4.81 (4.84)	7.50 (7.53)	8.55 (8.60)	8.76 (8.79)	10	Dia
17	Dark brown	280	34.69 (34.72)	2.01 (2.09)	11.51 (11.57)	13.20 (13.22)	12.05 (12.07)	-	Dia
18	Black	211	34.31 (34.39)	2.02 (2.05)	11.41 (11.46)	13.08 (13.10)	12.99 (13.00)	-	1.79
19	Brown	205	56.00 (56.00)	3.80 (3.82)	6.69 (6.70)	7.62 (7.66)	7.00 (7.02)	-	Dia.
20	Black	255	55.03 (55.67)	3.75 (3.80)	6.64 (6.66)	7.59 (7.61)	7.51 (7.55)	-	1.93

\*: Decomposition temperature, M: the corresponding metal

of the ligand to form the thiolate ion and the oxidation of the metal from M to M<sup>2+18</sup>. Treatment of the prepared complexes [M(L)<sub>2</sub>] with the diphosphine in (1:1) molar ratio gave new hybrid ligand complexes of the type [M(L)<sub>2</sub>Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>], n = 1-3, where as the dinuclear complexes were obtained from the reaction of the mononuclear complexes [M(L)<sub>2</sub>] with diphosphine in (2:2) molar ratio. In the hybrid ligand complexes of the type [M(L)<sub>2</sub>Ph<sub>2</sub>P(CH)<sub>n</sub>PPh<sub>2</sub>], the coordination was occurred through monodentate thiolate ion of the disulfide and for the diphosphine as a bidentate through both phosphorus atoms, while in the dinuclear complexes the diphosphine ligands acts as bridging between two metal in a bidentate fashion while for the thiolate ions as monodentate.

The analytical data of the ligand and its complexes are given in Table-1. These data were in a good agreement with the proposed formula. All these complexes are air stable at room temperature and insoluble in common organic solvents but they are soluble in dimethyl formamide or dimethyl sulfoxide.

The molar conductivity of 10<sup>-3</sup> M solution of the complexes indicate that they are non-electrolyte in DMSO<sup>19</sup>, also it was found that they are insulator in solid state, while the complexes of the type [M(L)<sub>2</sub>]I and [M(L)<sub>2</sub>Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>]I are (1:1) electrolyte. This is consistent with the stoichiometry for the complexes on the basis of analytical data.

The most important diagnostic feature of IR spectra of the complexes was listed in Table-2. The IR spectra of the ligand showed a characteristic bond due to  $\nu(\text{N-H})$  at 3250 cm<sup>-1</sup>, while the band due to  $\nu(\text{C=N})$  appeared at 1635 cm<sup>-1</sup> and  $\nu(\text{C-S})$  at 847, 984 cm<sup>-1</sup>, the  $\nu(\text{S-S})$  band appeared at 473 cm<sup>-120</sup>. In the complexes the  $\nu(\text{NH})$  band appeared at the same position indicating that this band was not shared in coordination, while the  $\nu(\text{S-S})$  band disappeared due to the cleavage

of this bond as discussed before. The  $\nu(\text{C-S})$  band observed at lower frequencies which indicate it was shared in coordination with the metal ions. Further support of this coordination is provided by the appearance of new band 380-360 cm<sup>-1</sup> which tentatively attributed to the  $\nu(\text{M-S})$ <sup>21</sup>. The  $\nu(\text{C=N})$  band of the ligand was shifted to a lower wavelength number and appeared in the region 1640-1610 cm<sup>-1</sup> in the spectra of metal complexes indicating coordination through the azomethine nitrogen atom to the metal atom. Formation of a metal nitrogen band was further supported by the presence of the band at about 575-535 cm<sup>-1</sup> for  $\nu(\text{M-N})$ <sup>22</sup>.

The IR spectra of diphosphine ligand showed a medium to strong band at 1100-1050 cm<sup>-1</sup>, which may be a signal to vibration of  $\nu(\text{C-P})$  group, the IR spectra of complexes showed new bands at 455-430 cm<sup>-1</sup> assigned to  $\nu(\text{M-P})$ <sup>23</sup>.

In order to obtain some information about the coordination properties of the metal ions, the electronic spectra has been recorded as 10<sup>-3</sup> M solution in DMSO and the results were presented in Table-2.

The bands observed at 39700-32258 cm<sup>-1</sup> (Table-2) due to disulfide ligand which may assigned to  $n-\pi^*$  or  $\pi-\pi^*$  transitions, respectively.

The magnetic moments of Ni(II) complexes **1**, **4-8** are 0.03 and 0.0 B.M which suggests square planer geometry around the nickel atom with D<sub>4h</sub> symmetry<sup>21</sup>.

The electronic spectra of mono and dinuclear Ni(II) complexes **1**, **4-8** showed two bands at 15772-16051 cm<sup>-1</sup> and 25510-26455 cm<sup>-1</sup> (Table-2). These bands were assigned to <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>A<sub>2g</sub> and <sup>1</sup>A<sub>1g</sub>→<sup>1</sup>E<sub>g</sub> transition. These results suggested square planer geometry around the nickel ion<sup>24</sup>.

The magnetic moments of mono and dinuclear Cu(II) complexes **2**, **9-13** has been found to be (2.20 and 1.63-2.08 B.M) which indicate the presence of one unpaired electron. The Cu(II) complexes **2** and **9** showed a band at 10162 cm<sup>-1</sup>

TABLE-2  
ELECTRONIC AND INFRARED SPECTRA DATA OF THE LIGAND AND THEIR COMPLEXES

No	Band maximum (cm <sup>-1</sup> ) $\lambda_{\max}$	IR band assignment (cm <sup>-1</sup> )					
		$\nu(\text{C-S})$	$\nu(\text{C=N})$	$\nu(\text{C-P})$	$\nu(\text{M-S})$	$\nu(\text{M-N})$	$\nu(\text{M-P})$
L1	322581, 39700	8475, 984 (m)	1635 s	-	-	-	-
1	15772, 26455	832(w)	1610 s	-	386 m	440 m	-
2	210162	835(w)	1595m	-	370 m	421 m	-
3	31446, 327827	830, 970	1590 m	-	364 m	430 m	-
4	15772, 260241	829 m	1635 m	1050 w	375 w	-	530 w
5	15923, 25906	830, 971	1637 m	1051 w	380 m	-	540 m
6	15898, 25773	825, 972	1637 m	1060 m	380 m	-	548 m
7	158229, 25641	830, 972	1637	1051 m	365 w	-	530
8	16051, 25510	810, 950	1637 w	1100 s	360 w	-	532 s
9	10204	820, 960	1635	1090 w	375 m	-	550 s
10	16286	962 m	1636	1080 w	389 w	-	533 m
11	16129	970 m	1637	1070 w	390 w	-	550 m
12	15974	810, 960	1637	1087	380 w	-	532
13	16000	810, 954	1635	1088	386 w	-	505
14	31645, 32787	960	1618	1080	380	428	499
15	30864	965	1616	1088	379	431	531
16	31446, 37037	830, 954	1610	1087	386	430	505
17	15772	830, 974	1636	1636	-	-	-
18	11250	810, 954	1636	1636	-	-	-
19	16051	810, 959	1637	1637	1090	-	520
20	10224	971	1636	1636	1100	-	519

and 10204 cm<sup>-1</sup> which are assigned to <sup>2</sup>T<sub>2</sub>→<sup>2</sup>E transition in tetrahedral environmental<sup>25</sup>, while the Cu(II) complexes (10-13) showed bands at 15974-16286 cm<sup>-1</sup> which were assigned to <sup>2</sup>B<sub>1g</sub>→<sup>2</sup>A<sub>2g</sub> and <sup>2</sup>B<sub>2g</sub>→<sup>2</sup>E<sub>g</sub> transition in distorted square planer geometry<sup>26</sup>.

The magnetic susceptibility measurements showed that all Zn(II) complexes **14-16** were diamagnetic and the electronic spectra of these complexes do not show any *d-d* band.

In the complexes of the formula [M(L)<sub>2</sub>]I and [M(L)<sub>2</sub>Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>]I, similar observation was found in the IR and UV/visible spectra expected to have a dark coloured complexes.

The electrical conductivities of the compact sample of the complexes were non conducting, the conductivity values in solid state are 1.3-9.61 × 10<sup>-12</sup> Ω<sup>-1</sup> cm<sup>-1</sup>, while the complexes of the type [M(L)<sub>2</sub>]I and [M(L)<sub>2</sub>Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>]I recorded in the temperature range 303-328 K showed that the complexes exhibit typical semiconducting behaviour. The conductivities of present complexes are well in the rang of 2.76-9.88 × 10<sup>-8</sup> Ω<sup>-1</sup> cm<sup>-1</sup> which similar to a number of transition metal containing polymers such as [M(C<sub>4</sub>S<sub>4</sub>)<sub>n</sub>], M = Ni(II) ions<sup>27</sup>.

The temperature dependent measurements of electrical conductivities of some of the complexes over the range 303-328 K, Fig. 1, indicate thermally activated conductivity.

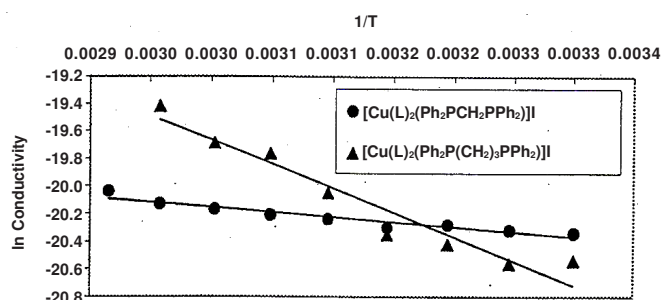
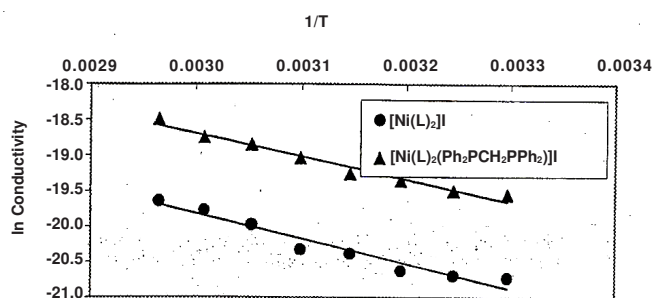


Fig. 1. Correlation between Ln conductivity and 1/T

The plot of log  $\sigma$  versus 1/T almost linear over this temperature range and the activation energy is low, Table-3. The increasing in electrical conductivities of these complexes with increasing of temperature shows the semi conducting properties of the complexes.

TABLE-3  
ACTIVATION ENERGY AND CONDUCTIVITY  
DATA FOR IODINATED COMPLEXES

No	Complexes	$\Lambda$ ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	Activation energy $\Delta E$ (KJ/mol)
17	[Ni(C <sub>7</sub> H <sub>5</sub> N <sub>2</sub> S <sub>2</sub> ) <sub>2</sub> ]I	3.10	2.9
18	[Cu(C <sub>7</sub> H <sub>5</sub> N <sub>2</sub> S <sub>2</sub> ) <sub>2</sub> ]I	3.39	6.12
19	[Ni(C <sub>7</sub> H <sub>5</sub> N <sub>2</sub> S <sub>2</sub> ) <sub>2</sub> (Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> )]I	9.88	2.6
20	[Cu(C <sub>7</sub> H <sub>5</sub> N <sub>2</sub> S <sub>2</sub> ) <sub>2</sub> (Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub> )]I	2.76	2.9

The band gaps evaluated from these plots and by using eqn. 1 were found to be low 2.6-6.12 KJ mol<sup>-1</sup> which is also indicative semi conducting behaviour.

$$\sigma = \sigma_0 e^{-\Delta E/KT} \quad (1)$$

The thiolate ligand used in this study, coordinated to metal ions in mono or bidentate fashion from thiolate sulfur atoms and azomethine group for mono nuclear complexes or from thiolate sulfur atom, where is the diphosphene coordinated in



bidentate fashion in mono nuclear and dinuclear complexes as shown in Fig. 2.

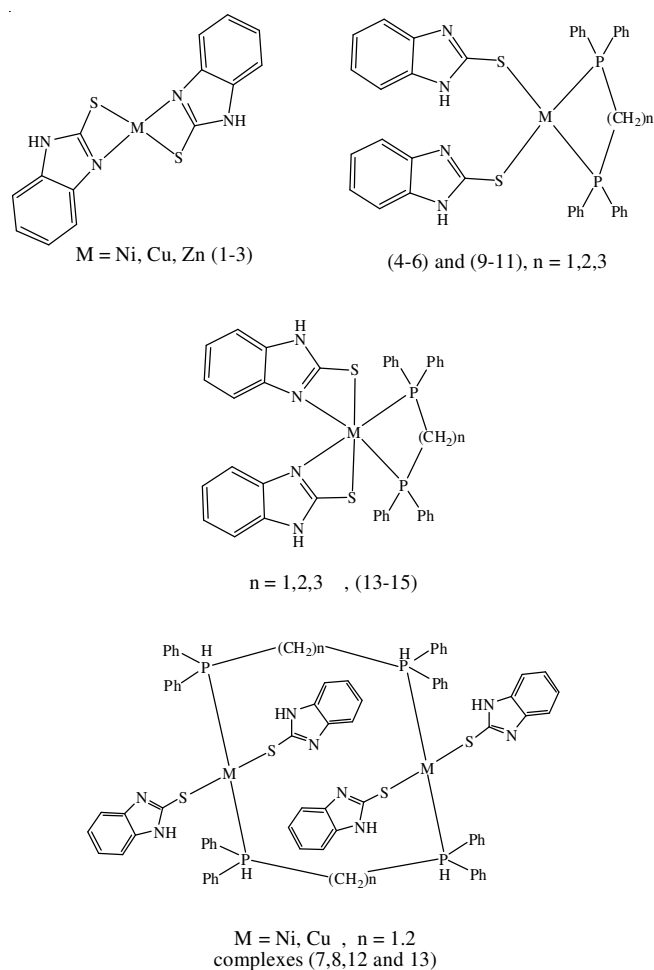


Fig. 2. Suggested structure for the complexes

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