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# Characterization, Thermal and Electrical Conductivity of some Transition Metal Adducts

Mohamed I. Ayad, Hanaa A. El- Boraey<sup>\*</sup>

Department of Chemistry, Faculty of Science, El-Menoufia University, Shebin El-Kom, Egypt.

# \*Corres.author: helboraey@yahoo.com

# Tel: 002-0111-7532777, Fax: +20482235689

**Abstract:** The well-established salen-type complexes  $[M(L^{I,II}](M = Co(II), Ni(II) \text{ or } Cu(II); L^{I} = N,N'-bis(o-hydroxynaphthyl)phenylene-1,2-diamine, L^{II} = N,N'-bis(o-hydroxynaphthyl)ethene-1,2-diamine or the binuclear Cu(II) complex <math>[Cu(L^{III})]_2(H_2L^{III} = 4-[3-(3-hydroxy-1-methyl-but-2-enylideneamino)-phenylimino]-pent-2-en-2-ol) interact as ligand with the main group halides; GaCl<sub>3</sub>, InCl<sub>3</sub>, SnCl<sub>4</sub>, or 4d- ZrCl<sub>4</sub> forming 1:1 or 1:2 heterometallic adducts. Characterization of these compounds was achieved using elemental analyses, molar conductivity, magnetic moments measurements, spectral (infrared, electronic, EPR) studies and thermal analysis. All these data reveal the adduct formation through the donor site of Schiff base O- atoms and the metal halides as an acceptor. The adduct decomposition starts with the dissociation of metal-halogen bond. The conductivity and activation energy were evaluated and found to depend on the molecular structure of the complex as well as the ionic potential of the metal ion.$ 

Key words: heterometallic complexes, EPR, electrical conductivity.

# Introduction

Multidentate Schiff bases have been widely used as ligands, because they can be easily attached to metal ions due to high stability of coordination compounds. The significant research efforts in the design and synthesis of heterometallic complexes are stimulated by their applications [1,2]. However, the formation of multimetallic transition metal complexes involving polydentate and compartmental ligands offers an important route for the construction of new types of magnetic materials, development of catalytic reagents models of metalloenzymes and the construction of metallo supramolecular architectures. In present days the polynuclear complexes are being used as luminescent compounds [2]. Transition metal complexes with tetradentate Schiff base ligands had been extensively investigated for the formation of heterodinuclear complexes of the type

(MZnL)(ClO<sub>4</sub>)<sub>2</sub>.nH<sub>2</sub>O (M = Cu, Ni or VO, L is a tetradentate Schiff base [2,3]. In order to construct such heterometallic complexes, one of the best strategies is the 'complex as ligand' approach, i.e., utilizing a metal complex (Schiff base metal complex) as a ligand to coordinate with an appropriate additional metal ion (main group halides) [4]. The adduct formation of zinc Schiff base complexes [Zn(2,3-salpyr)] and [Zn(3,4-salpyr)] where salpyr = N,N'-bis(salicylidene)-2,3- and 3,4-diiminopyridine as donor with some organotin chlorides as acceptors have been reported [5]. Synthesis and crystal structures of diimine complex of Cd(II) tetra hydroquinoline-dithiocarbamate and use of (1,10- phenanthroline) bis (1,2,3,4-tetrahydroquinoline-carbodithioato-S,S')-cadmium(II) for the preparation of CdS nanorods have been studied [6]. Novel azomethine adducts of Sn(IV) have been synthesized by the reaction of R<sub>n</sub>SnCl<sub>4</sub> (n = 1–3, R = CH<sub>3</sub>, *n*-C<sub>4</sub>H<sub>9</sub>, C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>11</sub>) with 2-((3,5-dimethylphenylimino)methyl) phenol (HL). The ligand and adducts have been screened for their biological activities, including DNA interaction, enzymatic, antibacterial, antifungal and cytotoxicity studies [7]. Complex formation of many organic compounds plays an important role in the field of conduction. An increase in the conductivity values is observed when metal ions are incorporated into the  $\pi$  electron delocalization of the organic compound. The reduction of conduction is noted if localized bond between metal ions and organic compound is created [8, 9].

In the present article the synthesis and characterization of molecular adducts resulting from the interaction of Ga(III), In(III), Sn(IV) and Zr(IV) chlorides with transition metal complexes *viz*. [M(L<sup>I,II</sup>] (M = Co(II), Ni(II) or Cu(II); L<sup>I</sup>=N,N'-bis(o-hydroxynaphthyl)phenylene-1,2-diamine, L<sup>II</sup>=N,N'-bis(o-hydroxy naphthyl) ethene-1,2-diamine or the binuclear Cu(II) complex [Cu<sub>2</sub>(L<sup>III</sup>)<sub>2</sub>] (H<sub>2</sub>L<sup>III</sup> = 4-[3-(3-hydroxy-1-methyl-but-2-enylideneamino)-phenylimino]pent-2-en-2-ol) have been studied by different analytical and spectral tools. The electrical conductivity as well as the activation energy of the current compounds was also evaluated.

## Experimental

#### Materials

2-hydroxy-1-naphthaldehyde, *o*-phenylendiamine, ethylenediamine, acetylacetone, tin tetrachloride, zirconium tetrachloride, indium trichloride, gallium trichloride, methanol, ethanol and DMF were obtained from Aldrich, and used without further purification.

## Synthesis of Compounds

The Schiff bases  $(L^{I}-L^{II})$  and their complexes with Cu(II), Co(II) and Ni(II) were prepared by the previously reported methods [10,11].

## Synthesis of adducts

The studied adducts were prepared by mixing and stirring the Schiff base complexes of Cu(II), Co(II) and Ni(II) as ligand with the respective metal chloride in dry chloroform under a dry nitrogen atmosphere in 1:1 or 1:2 (L:M) molar ratio. After several hours a bright solid (light-dark brown for copper, red for nickel and brown for cobalt) was obtained, filtered off, washed several times with dry chloroform and finally dried under vacuum over  $P_4O_{10}$ .

# **Physical Measurements**

All the synthesized compounds were analyzed for their C, H, N and Cl contents at Microanalytical Center, Cairo University, Giza. Metal content in the complexes and adducts was estimated by standard methods [12]. The molar conductance of the current compounds were performed on freshly prepared ( $10^{-3}$  M) DMF solution with a Ttoshniuval conductivity bridge. IR spectra were recorded as KBr discs on a Perkin-Elmer 598 Spectrophotometer (4000-200 cm<sup>-1</sup> range). UV-Vis. spectra were recorded in DMF solution using a Pye-Unicam Sp-8000 Spectrophotometer. Magnetic measurements were carried out at room temperature by Guoy's method. The EPR spectra were recorded using a Varian E-109C model X-band spectrometer. Thermogravimertic (TG) analyses were carried out using a Shimadzu DT-50 thermal analyzer with heating rate of 10 °C/min, the differential thermal analyses (DTA) were carried out in air using a Shimadzu XD-50 thermal analyzer, with heating rate of 10 °C/min and the sample weight was 12 mg. The electrical conductivity ( $\sigma$ ) of the compound were measured in air at the temperature range 35-100 °C using a super Magohmmeter

electrometer (model RM 170) the samples were pressed into discs of diameter 13 mm and thickness 1-3 mm under pressure of 300 kg cm<sup>-2</sup>. Good contact of electrodes with the surfaces of the disc was obtained by painting the surfaces carefully using silver paste. The temperature was measured using digital thermometer placed close to the sample. The currents (I) at different applied voltage (V) were measured at room temperature to establish the I-V characteristics of the metal complexes.

#### **Results and Discussion**

The prepared compounds were characterized by using various physical and analytical methods *viz*. elemental, molar conductance, magnetic susceptibility, IR, EPR and UV-Visible. All these data reveal the adduct formation through the donor site of Schiff base O- atoms and the metal halides as an acceptor. The elemental analyses and the molar conductivities for  $10^{-3}$  M DMF solution of compounds **1-12** are listed in Table 1. The conductance values are in the range 9.9-30  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> which is quite near to values for non-electrolytes in  $10^{-3}$  M DMF solution. This shows that they are stable and hence don't undergo ionization. Adducts **13**, **14** have limited solubility in DMF due to their dimeric nature.

As a result of adduct formation the azomethine frequency observed at 1620 cm<sup>-1</sup> in the parent Cu(II), Ni(II) and Co(II) complexes are shifted to higher frequency 1640-1630 cm<sup>-1</sup>, suggesting a steric strain in O-N-N-O sequence [2]. The phenolic oxygen v(C-O) observed at 1540-1550 cm<sup>-1</sup> in the parent complexes is shifted to higher (1565-1575 cm<sup>-1</sup>) frequency, suggesting that the phenolic oxygen are acting as the bridges in the current adducts [2]. The shift is generally considered as diagnostic of adduct formation [13]. The bands at 300–350 cm<sup>-1</sup> were assigned to the v(M\*–Cl) bond [7]. The adduct formation also supported by the appearance of a new band near 800 cm<sup>-1</sup> of di- oxo bridged ring vibration [14].

## **Magnetic Moments and Electronic Spectra**

The magnetic moments for adducts are **recorded in Table 1. The** values for the Cu(II) adducts are in the range 1.77 - 1.84 BM. These correspond to one unpaired electron. The appearance of only one band in the electronic spectra around 700 nm with two shoulders on either side at 540 and 860 nm is characteristic of distorted square-planar geometry [15]. The diamagnetic properties of all Ni(II) adducts indicated their square-planar geometry. The electronic spectra show that the absorption bands of Ni(II) complex occur around 520 and 410 nm. The lack of any electronic transition at longer wavelengths indicates large crystal-field splitting and is consistent with square-planar geometry for the Ni(II) complexes [16]. The observed magnetic moments of the Co(II) adducts fall within the range 2.58-2.68 BM, denoting low spin square planar Co(II) complexes. The electronic absorption spectra of these adducts have two bands around 660 and 600 nm characteristic of square-planar Co(II) complexes [17].

#### **Electron Paramagnetic Resonance Spectra**

The tensor value (g) of copper complexes can be used to derive the ground state. The X-band EPR spectra of  $[Cu(II)L^{I}]$  complex as well as its adducts **1,2,4** were recorded at room temperature using DPPH as a reference standard. All spectra are anisotropic and typically of axially symmetric monomeric Cu(II) complexes exhibiting distorted square planar geometry with  $g \parallel > g_{\perp}$  and  $d_{x_{2}-y_{2}}$  ground state [18].  $g \parallel$  values are 2.166 Cu(II)L<sup>I</sup>, 2.201(1), 2.201(2), 2.171(4). The  $g \parallel$  values are found to be nearly the same indicating that the bonding is dominating by the same coordination sites i.e NNOO. The  $g \parallel$  value is an important function for indicating covalent character of M-L bonds [19]; for ionic character  $g \parallel > 2.3$  while for covalent character  $g \parallel < 2.3$ . In the present compounds, the  $g \parallel$  is less than 2.3 indicating appreciable covalent character for the Cu-L bond.

#### **Thermal Studies**

The DTA curves of some selected adducts namely 1, 2, 4, 5, 8, 9 and 13 (Table 1S) show three exothermic peaks, the TG weight loss of the first stage corresponds to loss of chloride from  $M^*Cl_4$ , the second stage indicates the partial decomposition of organic ligand and the third stage corresponding to complete decomposition together with the formation of mixed metal oxide as final product. If the initial temperature of the decomposition step (Table 1S) is taken as a measure of the thermal stabilities of adducts, the following features can be observed:

i-The thermal stability for the adducts of the ligand  $L^{I}$  increases with increasing the atomic radii of transition metal (Fig.1) and follows the order, Cu(II) > Co(II) > Ni(II). The observed higher thermal stability of copper(II) adduct may be attributed to the fact that Co(II)-d<sup>7</sup> and Cu(II)-d<sup>9</sup> have ligand field stabilization energy due to Jahn–Teller effect. Also, Cu(II)-d<sup>9</sup> has more Jahn–Teller effect than Co(II)-d<sup>7</sup> [5].

ii-The lower thermal stability of the Cu(II)L<sup>II</sup> adduct **9** (300°C) compared to Cu(II)L<sup>I</sup> adduct **1** (320°C) may be attributed to the difference in diamine bridge i.e o-C<sub>6</sub>H<sub>4</sub>, compare to -CH<sub>2</sub>CH<sub>2</sub>- i.e., conjugation increases the thermal stability.

iii-  $L^{II}$  adduct **13** shows higher thermal stability than those of ligands  $L^{I}$  and  $L^{II}$ , i.e. (adducts **1** and **9**). This can be attributed to the dimeric structure of adduct **13** as well as the presence of four membered chelate rings with higher degree of conjugation [20]. Based on the above data, adducts structure may be formulated as follows: (Scheme 1).



1	$R = o-C_6H_4, M = Cu, M^* = Sn, x = Cl$
2	$\mathbf{R} = o\text{-}\mathbf{C}_{6}\mathbf{H}_{4}, \mathbf{M} = \mathbf{C}\mathbf{u}, \mathbf{M}^{*} = \mathbf{Z}\mathbf{r}, \mathbf{x} = \mathbf{C}\mathbf{l}$
3	$R = o-C_6H_4$ , $M = Cu$ , $M^* = Ga$ , $x = nil$
4	$\mathbf{R} = o - \mathbf{C}_6 \mathbf{H}_4,  \mathbf{M} = \mathbf{C}\mathbf{u},  \mathbf{M}^* = \mathbf{I}\mathbf{n},  \mathbf{x} = \mathbf{n}\mathbf{i}\mathbf{l}$
5	$\mathbf{R} = o\text{-}\mathbf{C}_{6}\mathbf{H}_{4}, \mathbf{M} = \mathbf{N}\mathbf{i}, \mathbf{M}^{*} = \mathbf{S}\mathbf{n}, \mathbf{x} = \mathbf{C}\mathbf{l}$
6	$\mathbf{R} = o\text{-}\mathbf{C}_{6}\mathbf{H}_{4}, \mathbf{M} = \mathbf{N}\mathbf{i}, \mathbf{M}^{*} = \mathbf{Z}\mathbf{r}, \mathbf{x} = \mathbf{C}\mathbf{l}$
7	$R = o-C_6H_4$ , $M = Ni$ , $M^* = In$ , $x = nil$
8	$R=\textit{o-}C_6H_4,M=Co,M^*=Sn,x=Cl$
9	$\mathbf{R} = -\mathbf{C}\mathbf{H}_2 - \mathbf{C}\mathbf{H}_2 -, \ \mathbf{M} = \mathbf{C}\mathbf{u}, \ \mathbf{M}^* = \mathbf{S}\mathbf{n}, \ \mathbf{x} = \mathbf{C}\mathbf{l}$
10	$\mathbf{R} = -\mathbf{C}\mathbf{H}_2 - \mathbf{C}\mathbf{H}_2 -, \mathbf{M} = \mathbf{C}\mathbf{u}, \mathbf{M}^* = \mathbf{I}\mathbf{n}, \mathbf{x} = \mathbf{n}\mathbf{i}\mathbf{l}$
11	$\mathbf{R} = -\mathbf{C}\mathbf{H}_2 - \mathbf{C}\mathbf{H}_2 -, \mathbf{M} = \mathbf{N}\mathbf{i}, \mathbf{M}^* = \mathbf{S}\mathbf{n}, \mathbf{x} = \mathbf{C}\mathbf{l}$
12	$\mathbf{R} = -\mathbf{C}\mathbf{H}_2 - \mathbf{C}\mathbf{H}_2 -, \ \mathbf{M} = \mathbf{C}\mathbf{o}, \ \mathbf{M}^* = \mathbf{S}\mathbf{n}, \ \mathbf{x} = \mathbf{C}\mathbf{l}$
13	$M = Cu(II), M^* = Sn(IV), x = Cl$
14	$M = Cu(II), M^* = In(III), x = nil$
-	

Scheme 1



No.	Formula	M.Wt	Analysis: Found (Calc) %				$\Lambda_{\mathrm{M}}$	$\mu_{eff}$	
			С	Н	N	Cl	M (Cu, Ni or Co)	$cm^2mol$	B.M.
1	CuL <sup>I</sup> SnCl <sub>4</sub>	738.23	45.2(45.5)	2.1(2.4)	3.4(3.78)	19.0(19.23)	8.2(8.6)	30.0	1.8
2	CuL <sup>1</sup> ZrCl <sub>4</sub>	710.76	47.4(47.3)	2.2(2.5)	3.7(3.9)	19.7(19.9)	8.7(8.9)	21	1.8
3	CuL <sup>I</sup> GaCl <sub>3</sub>	653.7	51.0(51.4)	2.5(2.7)	4.1(4.3)	16.1(16.3)	9.2(9.7)	23.3	1.83
4	CuL <sup>I</sup> InCl <sub>3</sub>	698.82	47.9(48.4)	2.4(2.6)	3.7(4.0)	14.8(15.2)	8.8(9.1)	27.8	1.81
5	NiL <sup>I</sup> SnCl <sub>4</sub>	733.31	45.6(45.8)	2.3(2.6)	3.3(3.8)	19.0(19.3)	7.4(8.0)	18	dia <sup>a</sup>
6	NiL <sup>l</sup> ZrCl <sub>4</sub>	705.93	47.2(47.6)	2.3(2.55)	3.8(4.0)	19.7(20.1)	7.9(8.32)	9.9	dia <sup>a</sup>
7	NiL <sup>I</sup> InCl <sub>3</sub>	694.03	48.0(48.4)	2.4(2.6)	3.7(4.03)	14.8(15.34)	8.3(8.5)	28.4	dia <sup>a</sup>
8	CoL <sup>1</sup> SnCl <sub>4</sub>	733.62	45.5(45.8)	2.5(2.6)	3.6(3.8)	18.8(19.3)	7.7(8.0)	27	2.64
9	CuL <sup>II</sup> SnCl <sub>4</sub>	690.23	41.5(41.7)	2.1(2.6)	3.7(4.0)	19.9(20.6)	8.8(9.2)	28.8	1.8
10	CuL <sup>II</sup> InCl <sub>3</sub>	650.86	43.8(44.2)	2.2(2.8)	3.9(4.3)	16.2(16.4)	9.6(9.8)	20	1.84
11	NiL <sup>II</sup> SnCl <sub>4</sub>	685.4	41.7(42.0)	2.3(2.6)	3.7(4.0)	20.2(20.7)	8.4(8.6)	15	dia <sup>a</sup>
12	CoL <sup>II</sup> SnCl <sub>4</sub>	685.62	41.8(42.0)	2.2(2.6)	3.9(4.1)	20.4(20.7)	8.2(8.6)	27.7	2.58
13	$(CuL^{III}SnCl_4)_2$	1186.2	32.0(32.3)	2.7(3.03)	4.2(4.7)	23.5(23.9)	10.4(10.7)	Part <sup>b</sup>	1.77
14	(CuL <sup>III</sup> InCl <sub>3</sub> ) <sub>2</sub>	1107.7	34.1(34.6)	2.8(3.24)	4.6(5.05)	18.7(19.2)	10.8(10.4)	Part <sup>b</sup>	1.78

Table 1. Analytical and Physical data of the adducts

<sup>a</sup> diamagnetic, <sup>b</sup> Partially soluble.

	Compound	Temp./ °C	TG Wt	TG Wt. loss %			
No.		*	Found	(Calc)	Reaction	Leaving species	
1	Cut IguCl	320	19.0)	(19.23)	d	-4Cl	
	CuL SnCl <sub>4</sub>	360	51.2	(51.7)	d	Loss of $L^{I} - O_{2}$	
		550	28.7	(29.02)	с	$\equiv Cu/SnO_2$	
2	Cul <sup>I</sup> ZrCl	300	19.7	(20.0)	d	-4Cl	
	Cull ZICI4	340	53.5	(53.75)	d	Loss of $L^{I} - O_{2}$	
		510	26.1	(26.32)	с	$\equiv Cu/ZrO_2$	
4	Cul <sup>I</sup> InCl	310	15.0	(15.2)	d	_	
	Cull IIICI3	325	54.3)	(54.7)	d	-3C1	
		470	29.7	(30.1)	с	Loss of $L^1 - O_2$	
						$\equiv Cu_2/In_2O_3$	
5	NH ISpC1	240	19.1	(19.36)	d	-4C1	
	NIL SIICI4	325	51.8	(52.1)	d	Loss of $L^1 - O_2$	
		520	28.4	(28.6)	с	$\equiv Ni/SnO_2$	
	Col <sup>I</sup> SpCl	280	19.1	(19.36)	d	-4Cl	
8	COL SIICI4	315	51.8)	(52.1)	d	Loss of $L^1 - O_2$	
		535	28.4	(28.6)	с	$\equiv Co/SnO_2$	
9		300	20.1	(20.6)	d	-4Cl	
	Cul SnCl <sub>4</sub>	330	48.4	(48.2)	d	Loss of $L^{II}$ - $O_2$	
		500	31.5	(31.04)	с	$\equiv Cu/SnO_2$	
13	(Cul <sup>III</sup> S nCl )	370	23.5	(23.9)	d	- -8Cl	
	(CuL $SnCl_4)_2$	440	39.6	39.9	d	Loss of $L^{III}$ - $2O_2$	
		590	36.9	36.6		$\equiv 2Cu/2SnO_2$	

 Table 1S. Thermal data of the adducts

\* exo, <sup>d</sup> decomposition, <sup>c</sup> Final product percent

# Fig. 1. Relationship between atomic radii (pm) of Co, Ni and Cu with dissociation temp./ $^{\circ}$ C



#### **Electrical Conductivity**

The variation of log  $\sigma$  with 1/T of the ligands and their parent copper(II) complexes as well as their adducts of Sn(IV), Zr(IV), Ga(IV) and In(III) are shown in Fig. 2. The conductivity  $\sigma$  variation with T is expressed by Arrhenius relation of the type Log  $\sigma = \sigma_0 \cdot \exp(-\Delta E/kT)$ .

Where  $\sigma_0$  is the pre-exponential constant corresponding to 1/T = 0,  $\Delta E$  is the activation energy of the electrical conductivity, T is the absolute temperature and k is the Boltzmann constant. It is evident that all compounds have a positive temperature coefficient of electrical conductivity  $(d\sigma/dT)$  [21]. Hence, all samples have semiconducting character within the investigated temperature range. The values of  $\Delta E$  and log  $\sigma$  at 50 °C are presented in Table 3. It can be seen that  $\Delta E$  values of the pure Schiff bases decreases in the order  $L^{I} < L^{II} <$  $L^{III}$ . This could be attributed to the decreased conjugation throughout the ligand. Therefore a delocalization of the  $\pi$  electrons would be enhanced and hence the activation energy for generation of carriers would be decreased [22,23]. After complexation,  $\Delta E$  values decreases and the conductivity increases comparing to that of free ligands, this may be due to the overlap between the electrons in the antibonding  $\pi$  orbitals of ligand, the empty *d*-orbitals of the transition metal cation. It leads to delocalization of the  $\pi$  electronic charges on the molecules. On dealing with the electrical properties of adducts in comparison with their pure complexes (Table 2, Fig.2). It can be seen that adducts have a specific behavior. The electrical conductivity of adducts with copper complexes of ligand L<sup>1</sup> goes on increasing with the increase in temperature on going from a pure metal complex to its adduct also the activation energy of trivalent ions is lower than the corresponding energy of tetravalent ions. In addition, the activation energy follows the order: Ga(III) < In(III) and Sn(IV) < Zr(IV) this is explained on the basis that the activation energy decreased with increasing ionic potential Z/r values {Sn(IV) = 57.1. Zr (IV) = 54.1 nm<sup>-1</sup>}, {Ga(III) = 48.4 and In(III) = 40.0 nm<sup>-1</sup>} [9.24], the activation energies of tri. tetravalent metal ion adducts with copper(II) complex of ligand L<sup>II</sup> is larger or slightly lower than that of their pure copper(II) complex. This is attributed to the molecular structure of adducts which affects the electron migration. It would be reasonable to suggest that their structure could localize the charge carriers, so that the  $\Delta E$ and  $\sigma$  values of In(III) adducts with copper complex of ligand L<sup>II</sup> were not enhanced towards semiconducting properties. The high  $\Delta E$  value obtained for the In(III) adduct of the copper(II) complex of ligand L<sup>III</sup> could be attributed to the same reasons discussed previously in the case In(III) adduct of the copper complex with ligand L<sup>II</sup>.

The log V - log I plots for the adducts of copper complex of ligand L<sup>I</sup> with Zr(IV), Ga(III), and In(III) are shown in Fig.3. It can be shown that the data fit the proportionality I  $\alpha$  V in the range of applied voltages 5< V< 400. This means that we have an ohmic conduction mechanism (i.e., the relation obeys Ohm's law; V = IR).



Fig. 2. Arrhenius plot of conductivity for Cu(II)L<sup>I</sup> adducts with Sn(IV),Zr(IV), In(III) and Ga(III) and for Cu(II)L<sup>III</sup> with In(III) adduct.

No.	Compound	$\Delta E(eV)$	$\text{Log } \sigma \left( \Omega^{-1} \text{cm}^{-1} \right)$
-	$L^1$	0.62	-12.64
-	CuL <sup>1</sup>	0.54	-12.48
1	CuL <sup>I</sup> SnCl <sub>4</sub>	0.42	-10.4
2	CuL <sup>I</sup> ZrCl <sub>4</sub>	0.48	-11.48
3	CuL <sup>I</sup> GaCl <sub>3</sub>	0.35	-11.9
4	CuL <sup>I</sup> InCl <sub>3</sub>	0.37	-10.48
-	$L^{\Pi}$	0.71	-11.7
-	CuL <sup>II</sup>	0.69	-11.2
9	CuL <sup>II</sup> SnCl <sub>4</sub>	0.62	-11.1
10	CuL <sup>II</sup> InCl <sub>3</sub>	0.86	-10.84
-	$\Gamma_{m}$	0.73	-10.4
14	$(CuL^{III} InCl_3)_2$	0.87	-10.4

Table 2.  $\Delta E$  (eV) and Log  $\sigma$  ( $\Omega^{-1}$ cm<sup>-1</sup>) values at 50 °C for different adducts



Fig. 3. LogV versus Log I for the Cu(II) L<sup>I</sup> adducts with Zr(IV), In(III) and Ga(III).

## Conclusions

The planar transition metal complexes *viz*.  $[M(L^{I,II}]$  (M = Co(II), Ni(II) or Cu(II), L<sup>I</sup> = N,N'-bis(*o*-hydroxynaphthyl) phenylene-1,2-diamine, L<sup>II</sup> = N,N'-bis(*o*-hydroxynaphthyl)ethene-1,2-diamine or the binuclear Cu(II) complex  $[Cu_2(L^{III})_2]$  (H<sub>2</sub>L<sup>III</sup> = 4-[3-(3-hydroxy-1-methyl-but-2-enylideneamino) phenylimino]-pent-2-en-2-ol) react as donor with Sn(IV), Zr(IV), In(III) and Ga(III) chlorides as acceptor, the above reaction result in the formation of 1:1 or 1:2 molecular adducts. The analytical and physicochemical analysis confirmed the composition and the structure of the obtained adducts. The results obtained can be summarized as follows:

- 1- Room temperature magnetic moment, electronic and EPR spectra data indicating retention of planarity about transition metal ion after adduct formation.
- 2- The EPR gll values indicate high energy d-d transition typical for planar Cu N<sub>2</sub>O<sub>2</sub> complexes.
- 3- The TG thermograms of adducts show no mass loss till decomposition, that starts with removal of chloride ions, indicating the absence of solvent/water molecules.

4- The activation energy  $\Delta E$  (eV) as well as conductivity Log  $\sigma$  ( $\Omega^{-1}$ cm<sup>-1</sup>) values for adducts and their parent complexes are significantly different.

# References

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