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Electrical conductivity of some amines and their non-transition metal complexes

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Abstract

The electrical conductivity of some heterocyclic amines and their complexes with Zn(II), Cd(II), Hg(II), As(III), Sb(III) and Bi(III) has been measured in the temperature range 290–450 K. The activation energy of conduction process, the charge carriers concentration and their mobility were calculated. The stoichiometry of complexes was determined by the help of conductometric and photometric titrations. The structure was studied using IR, TG-DTA and XRD techniques.

Keywords: Electrical conductivity; Heterocyclic amines; Non-transition metal complexes

1. Introduction

A large number of transition metal complexes with hydroxyquinoline derivatives [1,2] and aminohydroxypyridine [3,4] were prepared. The complexes were characterized potentiometrically and spectroscopy. However, only a small number of related non-transition metal complexes were reported [5]. Therefore, as a part of our study in search of some new metal organic conductors, the present paper deals with the electrical behaviour of some non-transition metal complexes of 8-hydroxyquinoline-5-sulfonic acid (HQSA) and 2-amino-3-hydroxypyridine (AHP). The composition of complexes was investigated by conductometric and photometric titrations, while their structure was characterized by IR, TG-DTA and XRD methods.

2. Experimental

All the chemicals used in this work were of high purity grade (Aldrich). In order to determine the stoichiometric ratio of different complexes, conductometric and photometric titrations were used. The conductometric titration curves were obtained by titrating 30 ml of 10^{-4} M aqueous solution of ligand (HQSA or AHP) against 10^{-2} M metal ion solution. A digital conductivity meter 5800-05 solution analyzer (Cole Parmer Instrument) was used. Photometric titration of non-transition metal ions and HQSA or AHP was carried out under fixed concentration of ligands (1×10^{-3} M) with various concentrations of each metal ion solution (0.25×10^{-3}–6.00×10^{-3} M). The spectrum was recorded using Milton Roy, Spectronic 1201, for each reaction mixture, then the absorbance was plotted as a function of the ratio of metal ion solutions added to the ligand solution in millilitres [6].

The solid complexes were prepared by refluxing equimolar amounts of the organic ligands, 10^{-2} M, and 10^{-2} M of chloride solutions of Zn(II), Cd(II), Hg(II), As(III), Sb(III) or Bi(III). A few drops of HCl were added to dissolve the different salts except in the case of zinc and cadmium chlorides. The reflux time was 4 h. The precipitated complexes were filtered off immediately after cooling, washed several times with ethanol then dried.

The IR spectra were recorded on a Shimadzu IR-440 spectrophotometer (300–5000 cm^{-1}). Thermal analysis (TG-DTA) were carried out under a nitrogen atmosphere using a STA-409 Netzsch DTA-TG analyzer in the range 20–500 °C with a uniform heating rate of 10 $°C\ min^{-1}$. XRD patterns were obtained with the aid of a Philips X-ray diffractometer PW 1390 fitted with an ionization detector (Cu $K\alpha$ radiation).

The electrical conductivity measurements, using a d.c. voltage of 10 volts across the cell, were carried out on discs of 13 mm diameter and 0.4 mm thickness sandwiched between two parallel copper electrodes [7]. The samples were molded at room temperature and under pressure of 4 ton cm^{-2}. A two terminal technique was employed using HC-3500 T and Thandar TM 353 multimeters.

3. Results and discussion

In principle, the conductometric titration is known to be one of many available analytical methods which has been

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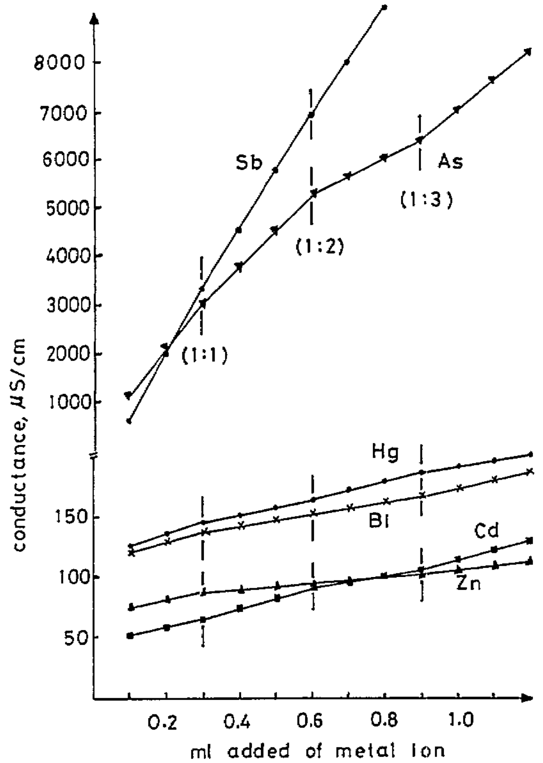

Fig. 1. Conductograms of HQSA with non-transition metal ions.

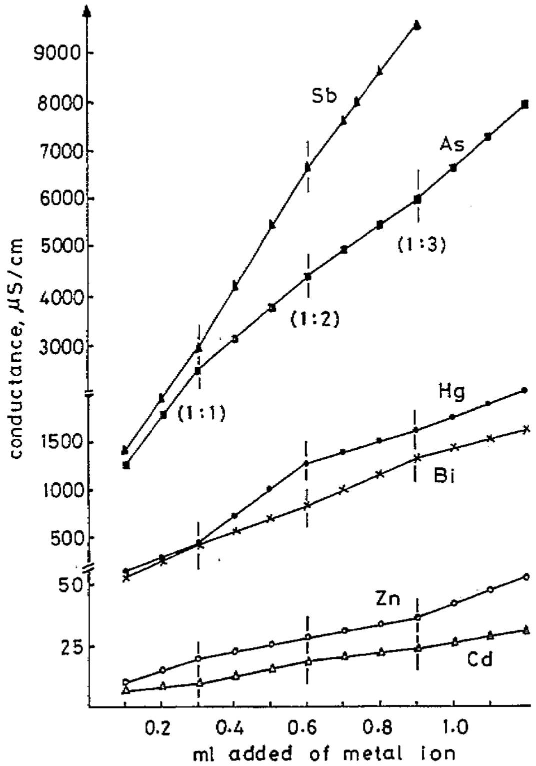

Fig. 2. Conductograms of AHP with non-transition metal ions.

widely used for determining the possible stoichiometric ratios for the complex formation [8]. The conductance of a solution is the sum of the individual conductivities of the dissolved ions. Thus, the conductometric titration can be used when the complex formation involves a change in the concentration of ions or when the ions are substituted by the other where their mobilities are different [9]. The conductograms are often complete in steps, i.e., the plots consist of some lines with different slopes. Consequently, each intersection gives a certain molar ratio of complex formation.

Fig. 1 shows the variation of conductance of HQSA aqueous solution as a function of millimetre additions of metal salt solution. The addition of metal ions to the ligand solution is accompanied by an increase of the conductance owing to the liberation of highly conducting hydrogen ions during the complex formation. The conductograms of HQSA complexes are characterized by three intersections, i.e., three molar ratios, 1:1, 1:2 and 1:3 (ligand:metal), are possible respectively.

The same behaviour was observed during the addition of metal salts to the solution of AHP, as shown in Fig. 2. The different breaks in the conductograms indicate that the probable stoichiometric ratios of AHP complexes are also, 1:1, 1:2 and 1:3. The conductometric titration data agree with the fact that both HQSA and AHP molecules have three centres capable of complexing with a metal ion.

The complexes studied are colored, thus their stoichiometric ratios can be determined more accurately by photometric titration than by conventional titration. A gradual change in the original color of the ligand (HQSA or AHP) is observed during the formation of the complex. An optimum wavelength is selected and a photometric reading is recorded for each incremental addition. Thus, the plot of absorbance versus the volume of titrant added to a fixed concentration of ligand will consist, if the reaction is complete, of two straight lines intersecting at the corresponding stoichiometric ratio [10].

The absorption band for free HQSA was found at 305 nm. On complexation, this band was shifted to 360 nm for the Bi complex and to 355 nm for the Hg complex. In the case of the AHP molecule, the absorption band was measured at 315 nm while after complexation, it was shifted to 305 nm. Fig. 3 shows the photometric titration of both Hg(III) and Bi(III) with each of HQSA and AHP. A similar behaviour was obtained for all complexes under investigation. It is clear that both amines form stable complexes with stoichiometric ratio 1:1, where the absorption did not change after adding 1 mole ratio of metal ion.

In light of the results obtained from the conductometric and photometric titrations, it is apparent that the more favorable stoichiometric ratio for both HQSA and AHP complexes is 1:1.

In order to get more information about the bonding sites in the complexes, the infrared spectra of the heterocyclic amines (HQSA and AHP) and the corresponding solid complexes (L:M) were recorded as shown in Fig. 4 and Fig. 5. The IR spectra of HQSA complexes display a strong and broad band at 3250 cm^{-1} which may be assigned to ν OH of coordinated water molecules. This is supported by the pres-

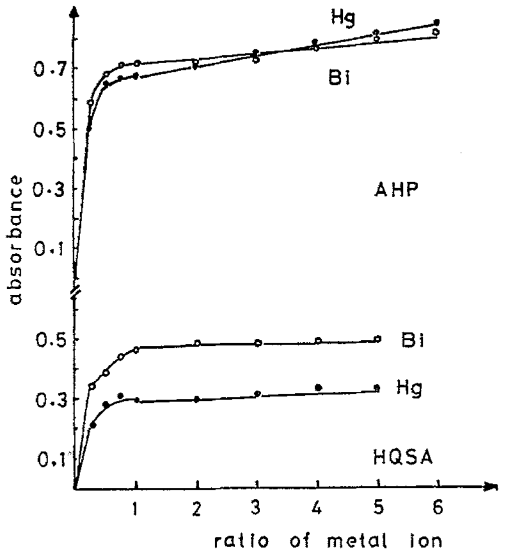

Fig. 3. Photometric titration curves for HQSA with Hg(II) and Bi(III) as well as AHP with Hg(II) and Bi(III).

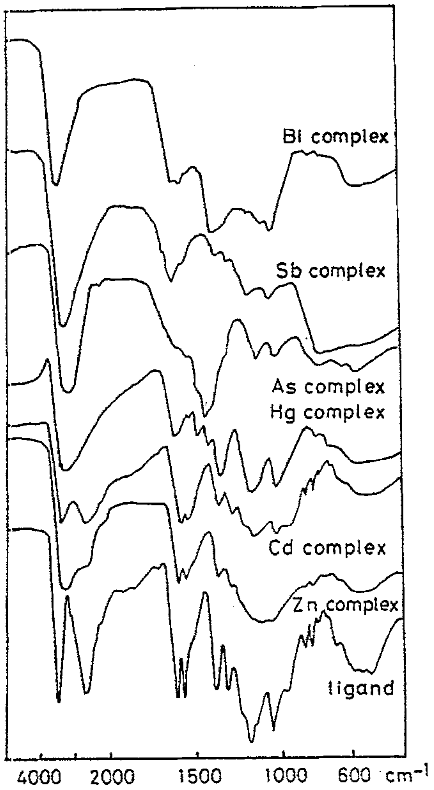

Fig. 4. IR spectra of HQSA and its complexes.

ence of bands around 750–840 cm^{-1} characteristic of H_2O wagging mode of vibration.

The IR spectrum of free HQSA molecules shows strong bands at 3500 and 2700 cm^{-1} which are attributed to the stretching vibration of phenolic OH engaged in intra-molecular hydrogen bonding OH...N [11]. The absence of the two bands after complexation indicates that the coordination of HQSA probably takes place through deprotonated phenolic oxygen.

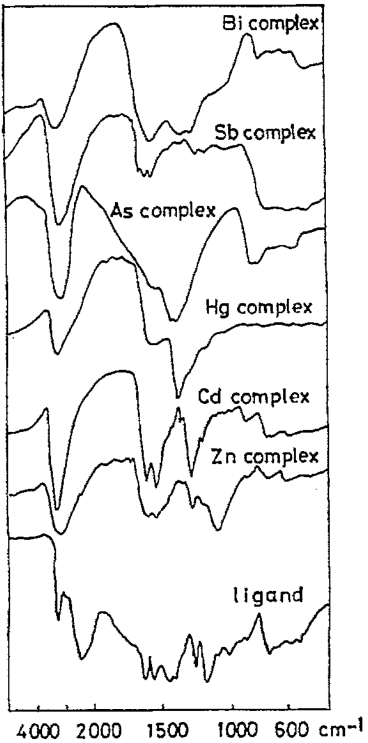

Fig. 5. IR spectra of AHP and its complexes.

The two sharp and strong bands at 1600 and 1570 cm^{-1} in the spectrum of HQSA may be attributed to ν C=N. The shift of both these vibrations by 10–20 cm^{-1} in the spectra of metal complexes demonstrates the bonding of the nitrogen atom of HQSA to the metal ion.

On the contrary, the strong absorption bands at 1180 and 1380 cm^{-1} which are assigned to symmetric and asymmetric stretching of S=O, respectively, remain unaltered in the spectra of complexes suggesting that the sulfonic group of HQSA does not take part in the coordination process [11,12]. This behaviour is in harmony with the fact that the sulfonic acid group is more acidic than the hydroxyl group owing to the greater stabilization of the sulfonate ion. The same trend was observed for chelation of 8-hydroxyquinoline with Al(III), Ga(III), In(III) and Tl(III) [13].

Fig. 5 shows the IR spectra of AHP and its complexes. All complexes display a strong and broad band at 3100 cm^{-1} which is assigned to the stretching vibration of the OH group of coordinated water molecules [14]. The spectrum of parent compound demonstrates a strong and sharp band at 3300 cm^{-1} which accounts for NH_2 stretching vibration and another strong and broad band at 2300 cm^{-1} corresponding to the intra-molecular hydrogen bonding. The disappearance of these bands in complexation is presumably owing to the drainage of electrons from the nitrogen atom towards the central metal ion. This is supported by the disappearance of a broad and medium band at 1460 cm^{-1} assignable to the bending vibration of the NH_2 group.

The shifting of the two absorption bands at 1620 and 1560 cm^{-1} (νC=N) to lower frequency after complexation sug-

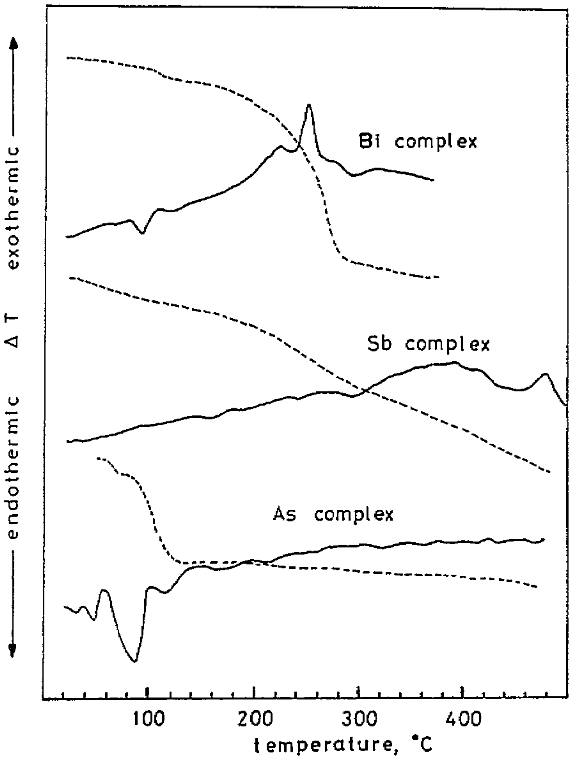

Fig. 6. Thermograms of some solid complexes with AHP. Solid line is DTA and dotted line is TG.

gests that the nitrogen atom of the pyridine ring is the second centre of chelation with the non-transition metal ions.

Consequently, on the basis of the above discussion, the HQSA molecule acts as NO donor, while the AHP molecule is NN donor.

Fig. 6 shows the thermal decomposition curves of some selected solid complexes of AHP. It is well known that the water of crystallization is more easily lost than that of coordination. The DTA curves demonstrate an endothermic peak around 90 °C which is attributed to the evolution of crystallized water (physically combined). A loss in weight corresponding to one molecule of water was found at about 5%. A weak endothermic peak appeared around 200 °C which is ascribed to the explusion of coordinated water. The exothermic peak within the temperature range 300–400 °C may correspond to the decomposition of the organic ligand AHP. The thermograms show at different temperatures a number of discontinuities owing to the formation of thermodynamically unstable intermediates.

Fig. 7 shows the X-ray diffraction patterns to identify the structure of complexes. The complex of arsenic with HQSA ligand was chosen for this work. It can be easily observe that the pattern of the organic ligand differs from that of its metal complex. The XRD peaks broaden after complexation owing to the formation of not well defined or distorted crystalline structure. This is attributed to the incorporation of water molecules in the coordination sphere.

To discuss the electrical characteristics of organic compounds (single crystal, polycrystalline or amorphous), the linear dependence of conductivity with increasing temperature was studied using the relation

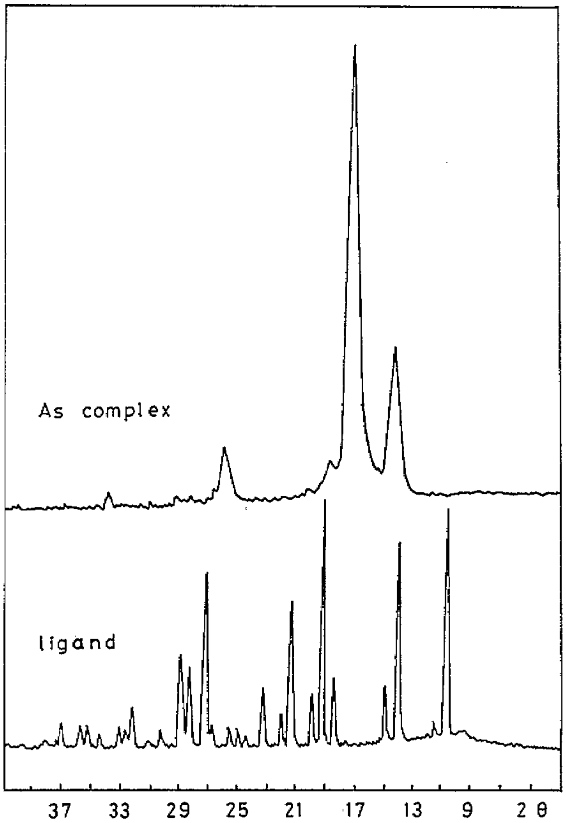

Fig. 7. XRD patterns of HQSA and its As complex.

$$\sigma = \sigma^{0} \exp(-E/KT)$$

where E is the activation energy of conduction. The plot of log σ versus $1/T$ of the amines and their complexes investigated are represented in Fig. 8 and Fig. 9. The results show that the conductivity value of HQSA is greater than that of AHP, at room temperature. In organic semiconductors, the conductivity is normally limited by the number of charge carriers, n, which depends on the temperature in the form

$$n = 2\left(\frac{2\pi m^{+} KT}{h^{2}}\right)^{3/2} \exp(-E/KT)$$

where m^{+} is the effective mass of charge carrier. The electrical data are reported in Table 1 and Table 2. It is clear that the charge carriers concentration of HQSA, 2.66×10^{23} cm^{-3}, is greater than that of AHP, 8.26×10^{17} cm^{-3}, i.e., the electrical conductivity of the first compound is greater than that of the last as obtained experimentally.

On the contrary, the conductivity of amines, in general, is increased after complexation owing to the inclusion of the metal ions into the pi electron delocalization of amines [15]. The stability of complexes leads to increase of the conductivity value. For non-transition metal ions, the stability of complexes normally increases with decreasing size of the cation [16], i.e.,

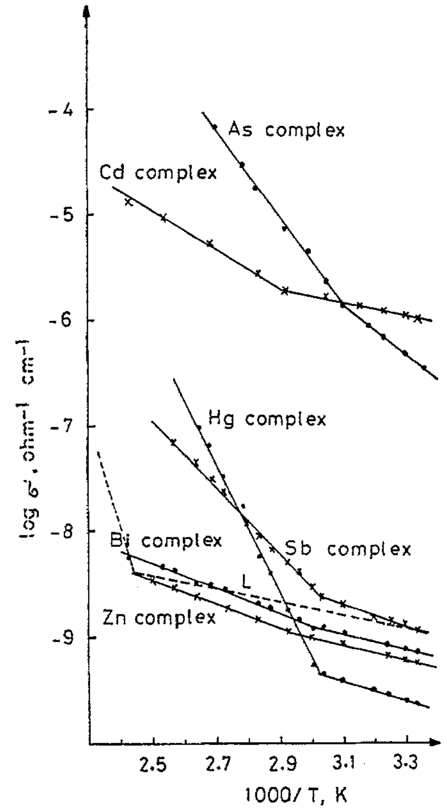

Fig. 8. Electrical conductivity of HQSA and its complexes.

$$As^{3+} (0.58\ Å) > Sb^{3+} (0.76\ Å) > Bi^{3+} (0.96\ Å)$$

$$Zn^{2+} (0.74\ Å) > Cd^{2+} (0.97\ Å) > Hg^{2+} (1.10\ Å)$$

The conductivity values obtained at room temperature obey this trend, except for the zinc complex.

It is of interest to indicate here that the electrical conductivity values of the non-transition metal complexes reported in this study are smaller than those previously reported for the transition metal complexes [17,18]. This is attributed to the fact that the transition metals form more stable complexes with organic ligands than the non-transitions.

If the interaction between charge carriers and lattice is strong, one is dealing with a small polaron (electron + lattice polarization). According to the Holstein model of small polarons [19], a phase transition is observed with rising temperature which is attributed to the change of conduction mechanism from band to hopping. All studied compounds exhibited this behaviour.

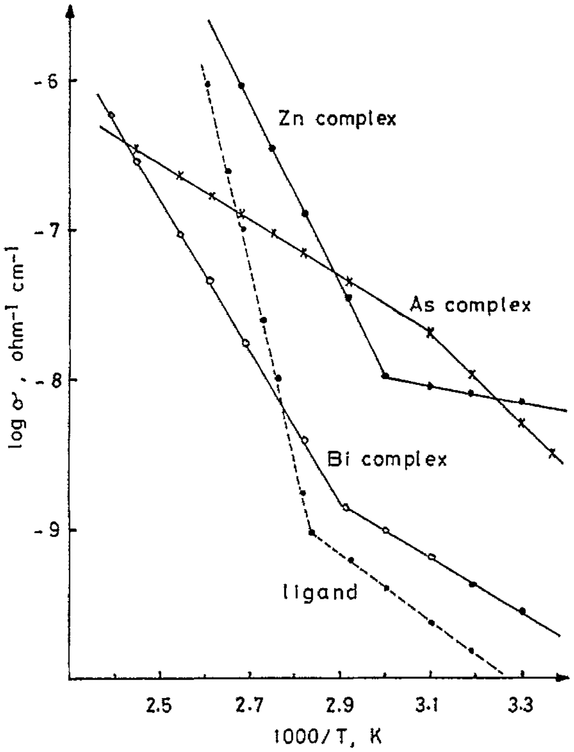

Fig. 9. Electrical conductivity of AHP and its complexes.

In order to clarify the conduction mechanism of the compounds investigated, the mobility of charge carriers, μ, was calculated using the basic equation

$$\sigma = ne\mu$$

where e is the charge of electron. It is apparent that the mobility of all studied compounds is very low which suggests that the conduction takes place by hopping mechanism [20].

In the hopping mechanism, the change of conductivity as a function of temperature can be written as

$$\sigma T = C \exp(-W/KT)$$

where C is a constant and W is the activation energy of the hopping process. The difference between W and E values gives the activation energy of mobility, E_μ. It is clear that E_μ for HQSA and its complexes (0.010–0.024 eV) is smaller than that for AHP and its complexes (0.024–0.039 eV), sug-

Table 1
Electrical data of HQSA and its complexes at 303 K

Compound	σ (ohm^{-1} cm^{-1})	E (eV)	W (eV)	n (cm^{-3})	μ (cm^2/V s^{-1})
HQSA	1.20×10^{-9}	0.119	0.139	2.66×10^{23}	2.96×10^{-14}
L:Zn	5.82×10^{-10}	0.148	0.158	8.76×10^{22}	4.15×10^{-14}
L:Cd	1.15×10^{-6}	0.119	0.139	2.66×10^{23}	2.58×10^{-11}
L:Hg	2.40×10^{-10}	0.182	0.198	2.38×10^{22}	6.30×10^{-14}
L:As	4.08×10^{-7}	0.475	0.495	3.17×10^{17}	7.80×10^{-6}
L:Sb	1.26×10^{-9}	0.198	0.218	1.29×10^{22}	6.10×10^{-13}
L:Bi	7.24×10^{-10}	0.154	0.178	6.96×10^{22}	6.50×10^{-14}

Table 2
Electrical data of AHP and its complexes at 303 K

Compound	σ (ohm^{-1} cm^{-1})	E (eV)	W (eV)	n (cm^{-3})	μ (cm^2/V s^{-1})
AHP	8.51×10^{-11}	0.45	0.475	8.26×10^{17}	6.44×10^{-10}
L:Zn	7.16×10^{-9}	0.10	0.139	5.51×10^{23}	8.12×10^{-14}
L:As	5.13×10^{-9}	0.59	0.614	3.87×10^{15}	8.20×10^{-6}
L:Bi	2.75×10^{-10}	0.36	0.384	2.60×10^{19}	6.61×10^{-11}

gesting that the electrical conductivity values of the first series of compounds are greater than those of the second series.

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