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DC electrical conductivity of poly[4-amino-2,6-pyrimidinodithiocarbamate] and its metal complexes

Ali El-Shekeil[a,]*, Hussein Al-Maydama[a], Ashour Al-Karbooly[a], Maarib A. Khalid[b]

[a]*Chemistry Department, Faculty of Science, Sana'a University, PO Box 12463, Sana'a, Yemen*
[b]*Physics Department, Faculty of Science, Sana'a University, PO Box 12463, Sana'a, Yemen*

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Abstract

Poly[4-amino-2,6-pyrimidinodithiocarbamate] (PPT) is prepared from the reaction of 2-mercapto-4,6-diaminopyrimidine with carbon disulfide followed by condensation through the removal of H_2S gas. The polymer is then used as a ligand to form polymer–metal complexes with the 3d-elements Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II). The DC electrical conductivity as a function of temperature is measured in the temperature range 300–500 K. The mechanism of conduction, the role of adsorbed water and complexation are explained on an energy diagram. This is carried out in accordance with the u.v.–VIS spectrum, TGA and DTA measurements. For comparison with 5d-elements, measurements are carried out also on Hg(II)–polymer complex. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polydithiocarbamate; Polydithiocarbamate complexes; DC electrical conductivity

1. Introduction

The demand for high performance polymeric materials in different fields of application has led to many publications in the past 50 years. Special cases of much interest are polymers containing metallic ions (either as a dopant or as complexes). These attracted the attention of researchers for a variety of reasons [1–9].

In the present work, we present a comparative study of some polymeric complexes from the point of view of the DC electrical conductivity and its change with temperature. Poly[4-amino-2,6-pyrimidinodithiocarbamate] (PPT) is chosen as our objective polymer due to its characteristic structure. The polymer contains nitrogen and sulfur atoms, which are rich in electrons. It is hoped that such atoms will facilitate the conjugated chain's concept and hence enhance electrical conductivity through the chain [9]. Also, the existence of this excess of electrons on the polymeric chain will allow this polymer to act as a polymeric ligand around the metal ion forming the desired complex. The unattached electron pairs on the nitrogen and sulfur atoms of the polymer can coordinate with the metal ion. On the other hand, this polymer is highly polar and hence it is plagued with water adsorbance, either in its uncomplexed or complexed forms. This will give us the opportunity to study the effect of adsorbed water on the DC electric conductivity. We choose for the complex-ions the 3d-transition elements: Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II). This choice may shed some light on the effect of the 3d-electrons on the π electrons of the polymer main chain or visa versa. To test the proposed mechanism, the Hg(II) complex, as an example of the 5d-elements, is compared with the Zn(II) complex.

2. Experimental

2.1. Synthesis of polymer and polymer complexes

Complete details of the synthesis are published elsewhere [10,11]. The polymer and polymer complexes used in this study are prepared according to Scheme 1.

2.2. Measurements

For electric DC conductivity, samples of 200 mg were thoroughly ground and pressed into circular discs of 12.5 mm diameter and thickness between 0.8 and 1 mm under 10^4 kg cm^{-2} pressure. To ensure good conductivity contact, the two surfaces of the discs were covered with conducting silver paste (FSP 51, Johnson Matthey and Co., UK). More experimental details are given elsewhere [12].

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* Corresponding author.

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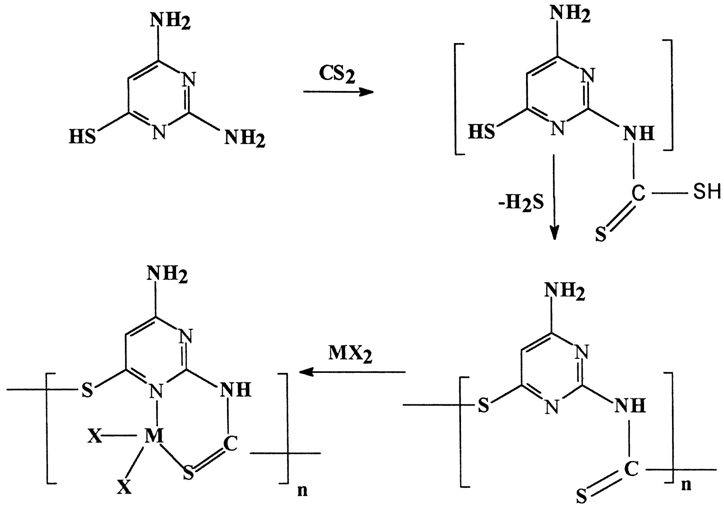

M = Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Hg(II)

Scheme 1. Synthesis of PPT and its complexes.

The TGA and DTA thermograms were obtained using STA 1500 + instrument, at a heating rate of 10°C/min, under a nitrogen stream.

3. Results and discussion

3.1. Characterization

The polymer prepared had an inherent viscosity of 0.39 and was found to be soluble in DMSO and partially soluble in DMF. The polymer complexes were found to be insoluble in all common organic solvents attempted. The melting point of the polymer and its complexes is > 300°C.

Table 1 shows some relevant characters of the compounds subjected to the investigation. The formula of each compound in Table 1 indicates the coordinated water with the adsorbed ones. The adsorbed water, one expects, may play some role in the physical characteristics of these compounds with temperature variation.

3.2. I.r. spectra

Fig. 1 shows the i.r. spectra of PPT and some of the complexes. The similarity of the complexes in the region (3200–3500 cm^{-1}) — i.e. the coordinating water band region — is clear enough from the figure. On the other hand, there are some modifications in the finger print region [13].

3.3. u.v.–VIS spectra

Fig. 2 shows the electronic spectra of PPT with other typical ones of some complexes. One cannot fail to notice that the spectrum of PPT has a clear cutoff at about 360 nm wavelength (corresponds approximately to 3.4 eV). On the other hand, the spectra of the complexes extend further into the visible region. Some of them even have bands in the far-red region (600–800 nm). This is expected with the absorption spectra of complexes [4]–[16]. So, we obtain the different colours of the complexes as shown in Table 1.

Table 1
The physical data of polypyrimidinodithiocarbamate and its complexes

Polymer	F. Wt.	M% Calc. (Found)	N% Calc. (Found)	Yield%	Color	μ_{eff}
PPT $C_5H_4N_4S_2{\cdot}2H_20$	220	—	24.9 (25.4)	74	Yellow	—
PPT-Mn $C_5H_4N_4S_2Cl_2Mn{\cdot}4H_2O$	382	13.8 (14.4)	16.1 (14.6)	41	Brown	5.91
PPT-Fe(II) $C_5H_4N_4S_2Cl_2Fe{\cdot}4H_2O$	383	15.3 (14.6)	14.0 (14.6)	52	Dark brown	4.70
PPT-Fe(III) $C_5H_4N_4S_2Cl_3Fe$	346.5	15.7 (16.2)	15.1 (16.2)	68	Dark brown	5.82
PPT-Co $C_5H_3N_4S_2Cl_2Co{\cdot}4H_2O$	385	15.3 (14.8)	14.5 (14.9)	86	Dark green	2.28
PPT-Ni $C_5H_3N_4S_2Cl_2Ni{\cdot}2.5H_2O$	358	16.5 (15.3)	15.6 (14.2)	79	Dark brown	2.91
PPT-Cu $C_9H_{10}ON_4S_20_4Cu{\cdot}6H_2O$	473.5	13.4 (11.0)	11.4 (8.99)	42	Brown	1.68
PPT-Zn $C_5H_4N_4S_2Cl_2Zn{\cdot}4H_2O$	392.5	15.8 (16.7)	15.3 (14.3)	89	Light brown	[a]
PPT-Hg $C_5H_4N_4S_2Cl_2Hg{\cdot}4H_2O$	527.6	36.3 (38.0)	19.8 (10.6)	90	Black	[a]

[a] Diamagnetic.

In accordance with the PPT spectrum, we can assume the value of 3.4 eV as the energy gap between the highest occupied molecular orbitals (usually we take it as the π levels) and the lowest unoccupied ones.

Fig. 3 shows the position of the bands' peaks as apparent from the optical spectra. The existence of such bands beyond the 365 nm cutoff of the polymer itself is clear. This indicates the presence of occupied levels in the polymer energy gap [9].

4. Thermograms

In our study of the DC electrical conductivity, the specimens were subjected to temperature changes. Hence, a change in the composition, if any, may lead to changes of the measured quantities. For this reason, the compounds under study were subjected to thermal analyses (TGA and DTA). As indicated from these analyses the loss of the adsorbed water can begin from room temperature. PPT and its Fe, Co and Zn complexes lose two molecules of the adsorbed water before 150°C in one step. On the other hand, the Cu-complex loses its adsorbed water in two steps. (at 80.68°C and then at 132.67°C), two molecules in each step. One can then infer that these adsorbed water molecules in the two steps are not equivalent with respect to their attachment to the compound. The Ni-complex loses about 1.5 molecules in two steps. It is to be noted that in all cases the loss of water is exothermic! Could this interesting phenomenon be caused by a relaxation process of the polymer's chain or perhaps it is attributable to the energy difference in different tautomeric configurations [17]? It cannot be interpreted as a breakage of a hydrogen bond or an electrostatic attraction. The correspondence between the thermograms and the DC electrical conductivity will be discussed later.

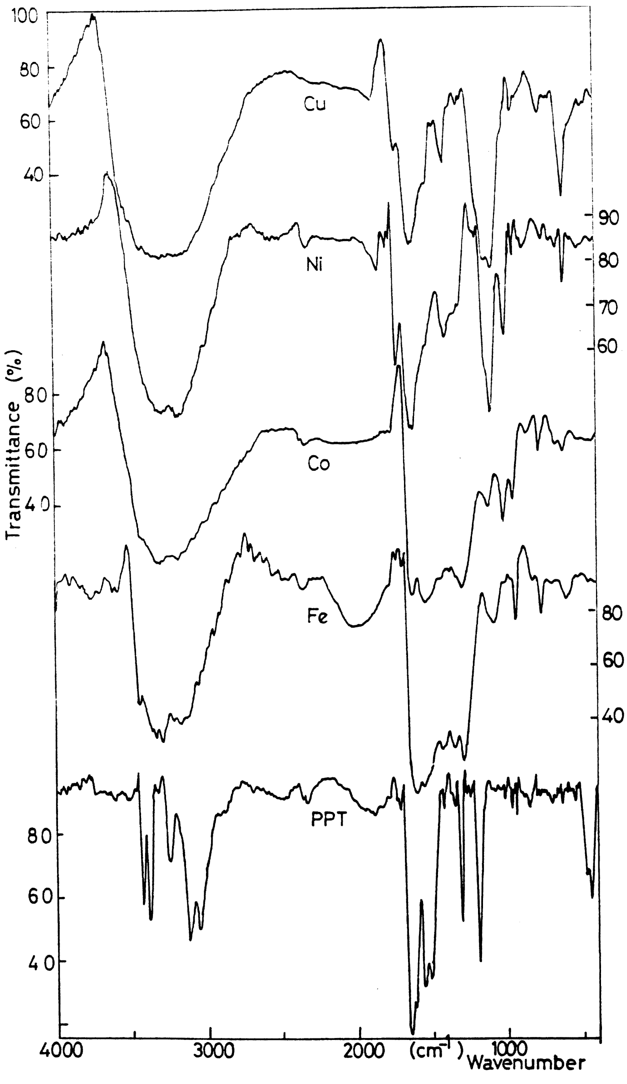

Fig. 1. I.r. spectra for PPT and some of its complexes.

5. The electrical conductivity

5.1. The polymer and its 3d-complexes

Fig. 4 presents the behaviour of log σ vs $1/T$ for PPT and its complexes. From the first impression, there seems to be no common feature of the different compounds. But, on close inspection general features stand out from the curves:

1. Almost all the curves show what can be called the reclining chair figure, otherwise; a step-wise behaviour.
2. As a general feature, complexation lowers the conductivity value of the compound, except in the case of Cu(II).
3. In the high temperature region, above 110°C, the activation energy of the complexes are the same (~1.7 eV) which is half the value of PPT itself (~3.4 eV).

We begin with the high temperature region, (above 110°C). The activation energy for PPT in that region is comparable to the value of the molecular cut off energy obtained from the u.v.–visible molecular spectra mentioned above. Thus, one can assume that the bulk 'van der Waals' gap in the centered material (i.e. the discs) [18] between the upper limit of the bulk valence band (chemically: the bonding orbitals) and the lower limit of the bulk conducting band (chemically: the anti-bonding orbitals) is not far in value from the molecular one [18]. This is due to the high polarity of the polymer itself.

On the other hand, the activation energy for the complexes in the same region is 1.7 eV. This corresponds to the mid-point of the bulk van der Waals gap [18]. If one is to remember that the non-bonding states are in the middle of the energy gap [9], one can then assume that by complexation the mid-gap states are occupied. And this will take care of the high temperature segment of the curves of the complexes.

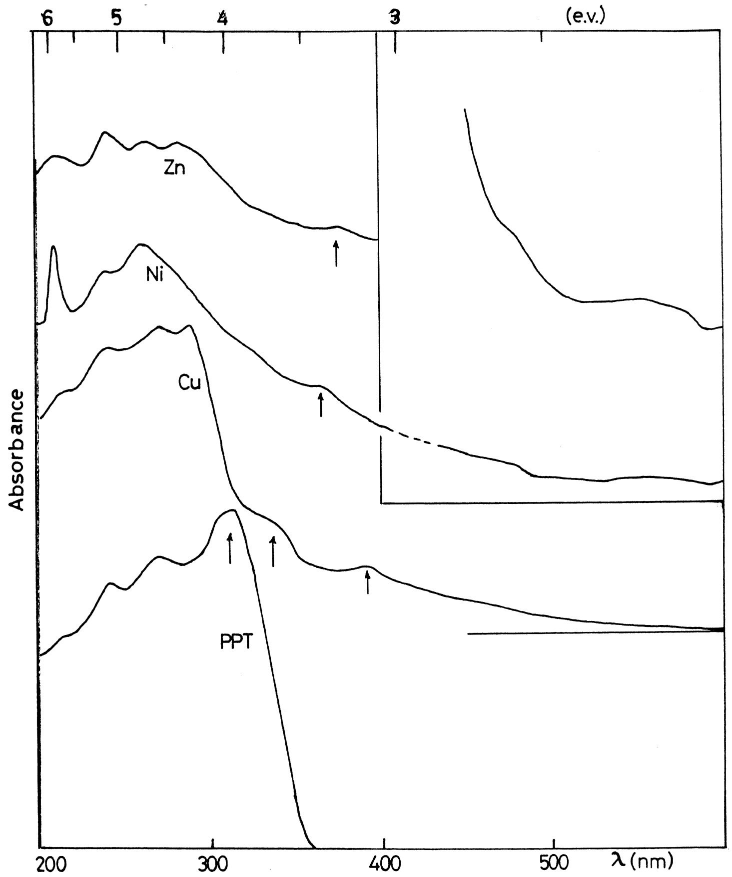

Fig. 2. The electron spectra of PPT and some of its complexes. The insert shows the amplified portion of Ni complex. All the complexes have absorption spectra in the visible region. The arrows indicate the apparent peaks of the transition band as shown in Fig. 3.

In the lower temperature region (i.e. below 110°C), there is a loss of the adsorbed water as confirmed by the TGA and DTA results. This is associated with an increase in the electrical conductivity. This is shown schematically in Fig. 5. The activation energy is less than the high temperature region's values either in the case of PPT or its complexes. So, the question is whether there is any relation between the release of the adsorbed water and the activation energy's values? The answer can be found by a comparison, between the behaviour of the two iron complexes: Fe(II) and Fe(III) shown in Fig. 6.

The Fe(III) complex has no adsorbed water and its curve is simple. It consists of two segments only: (i) a temperature independent segment (30–120°C) where the electron–phonon interaction is negligible and the number of carriers is temperature independent, i.e. the number of

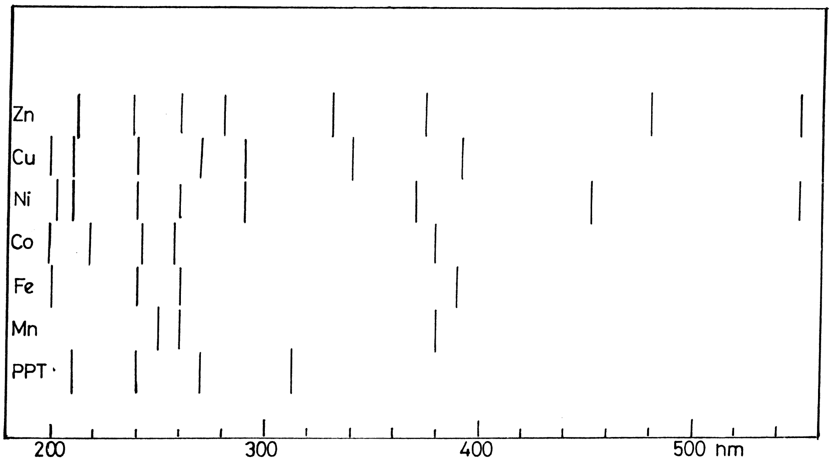

Fig. 3. Estimated apparent peaks of the transmission bands for the PPT and its complexes. One can observe some similarity as for example about 400 nm.

carriers is constant. And then (ii) the intrinsic conductivity segment ($>$ 120°C) with activation energy equal to 1.7 eV.

On the other hand, the Fe(II) complex (which contains adsorbed water) has three different segments. The first segment ($<$ 30°C) is a temperature independent one with the same value of conductivity more or less as the Fe(III) complex. In the second segment (30–110°C), in which it loses its adsorbed water, we have an increase in electrical conductivity with activation energy equal to 0.3 eV. In the third segment ($>$ 110°C), after it got rid of the adsorbed water, it follows its intrinsic region as in the case of Fe(III) with activation energy equal to 1.7 eV.

Let us try to understand this behaviour by assuming the existence of a soliton state ($S°$) beside the non-bonding states mentioned before. The creation of this soliton ($S°$) is due to either complexation or adsorption of water. It leaves a hole in the valence band (chemically: the bonding band) and an electron (trapped) in the soliton state [9]. It will take 1.7 eV to create this hole. Heat will excite this soliton's electron to the conduction band (the electron will gain 1.7 eV) and thus it will be free to move. It either recombines with one of the solitons' holes or contributes to the number of the conductivity carriers. In the first instant (below 110°C) the electron loses its energy as a result of such a recombination. The activation energy (E_a) as a result would be zero. In the second case (above 110°C), we have a rise in the electric conductivity with activation energy equal to 1.7 eV. This explains completely the Fe(III) complex behaviour.

Also, suppose we assume the existence of a polaron ($P°$)

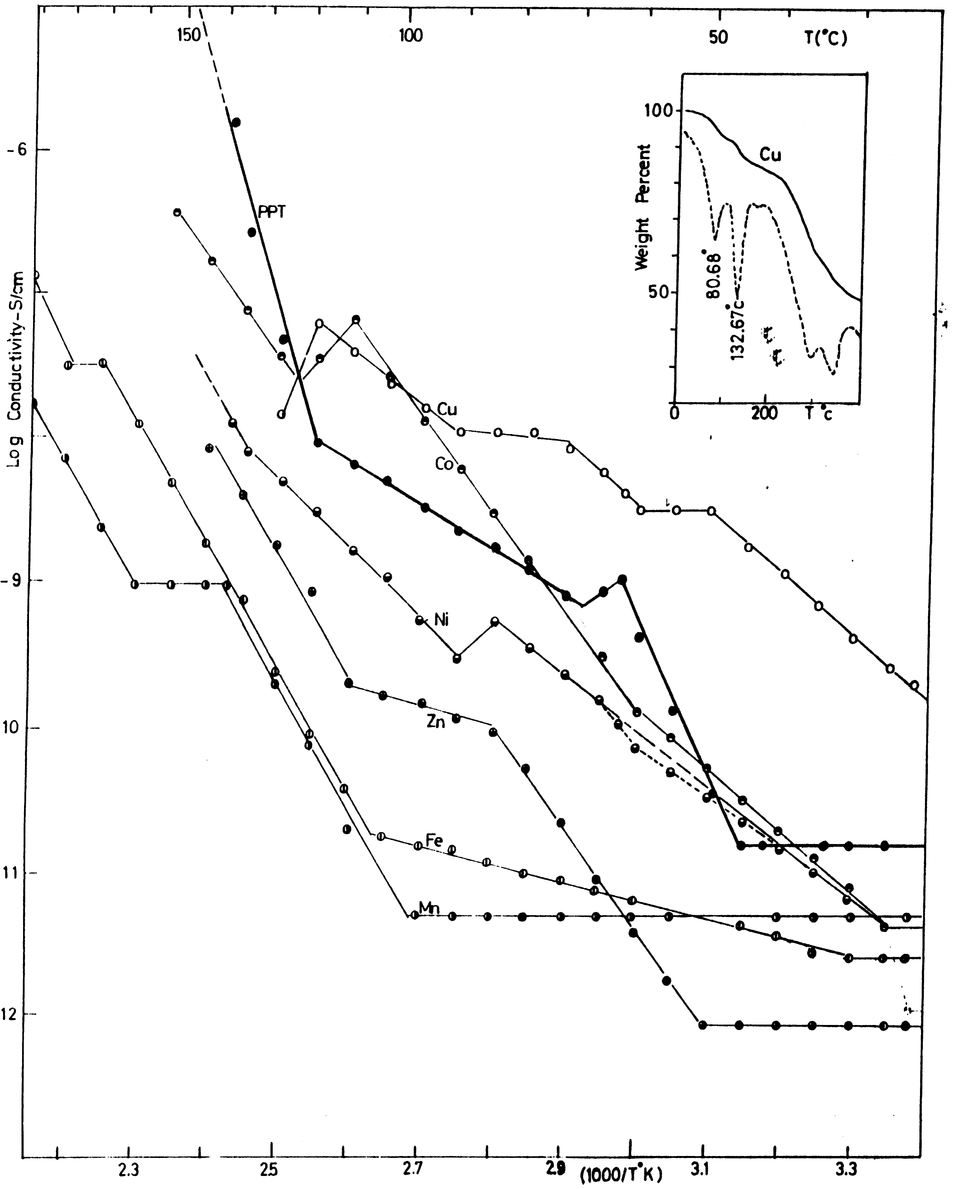

Fig. 4. The log conductivity versus $1/T$ curves for the polymer and its complexes in the region 30–190°C. The insert is a portion of the TGA thermogram for the Cu complex as a typical example of the behaviour of the complexes.

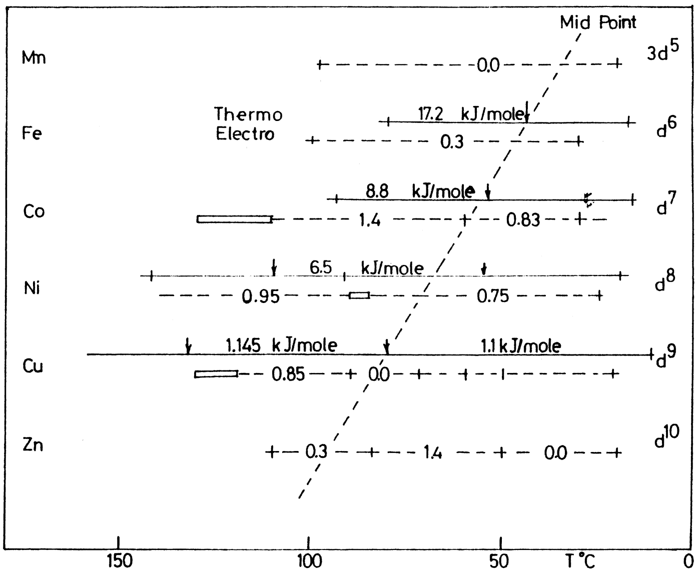

Fig. 5. A schematic diagram showing the association between the thermal and the DC electric conductivity. The numbers on the thermal lines are the value of the energy associated with the exothermic process. Notice that the values decrease as one goes down. The arrows indicate the position of the peaks as shown in the insert in Fig. 4. The numbers on the electric lines are the activation energies (eV). The white rectangles indicate the positive activation energy on the curves in Fig. 4.

at 2 eV from the bottom of the conduction band. In other words, it will be 1.4 eV from the top of the valence band. One has to remember that in the case of trans-ployacetylene, a polaron needs only 0.65 eV, which is less than 0.7 eV (half the energy gap) needed to form a hole in the valence band [9]. The existence of this polaron state is due to the introduction of the adsorbed water to the compound. On raising the temperature of the sample two things take place: (i) the adsorbed water leaves the sample, and as a sequence; and (ii) the uppermost inner-gap electrons go to the bulk conduction band and become free. The first ones to go, in our case, are the mid-gap states' electrons.

First, they recombine with the exitons' holes with zero activation energy. This is the first segment in the curve of Fe(II). Second, they recombine with polarons' holes. Now if the two processes, activation and recombination, can be

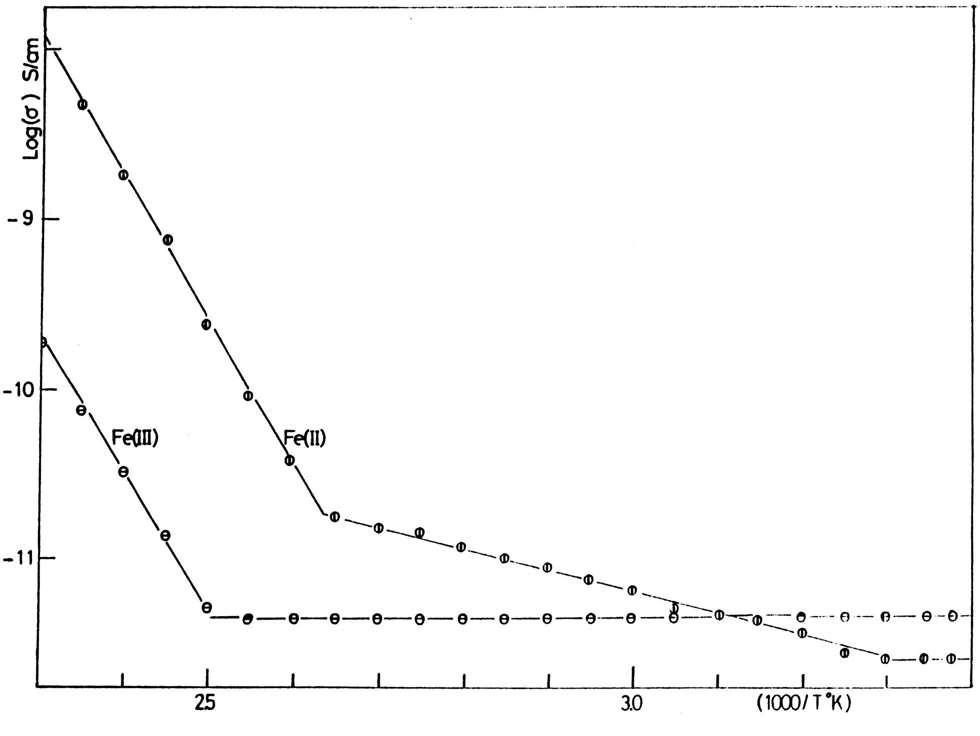

Fig. 6. A comparison between Fe(II) and Fe(III) complexes with regard to the increase of electrical conductivity with temperature.

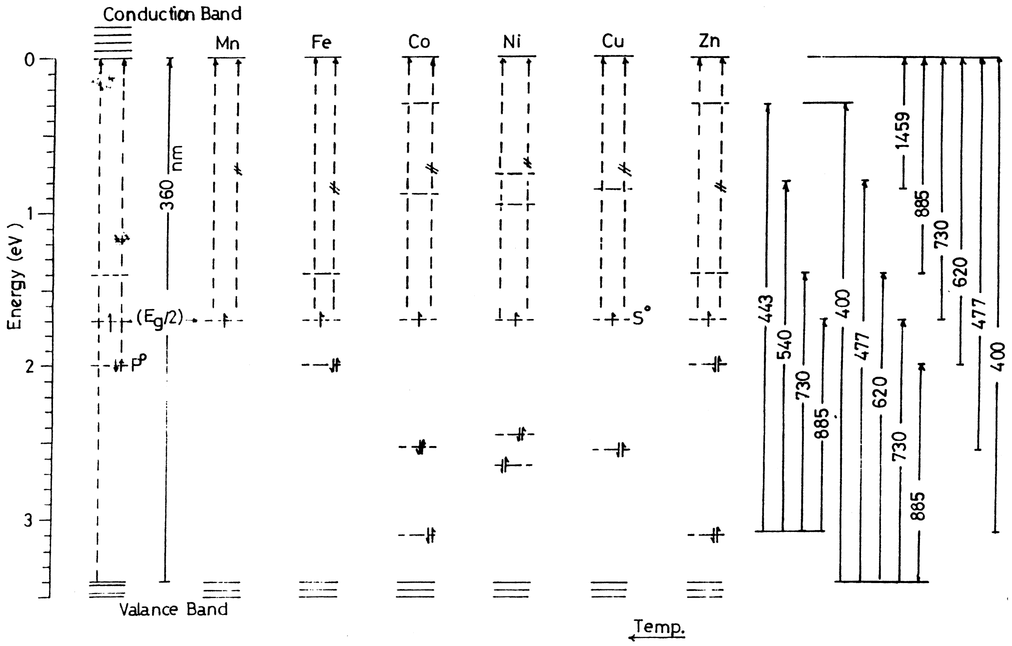

Fig. 7. The proposed energy band diagram for the polymer and its complexes. The transitions [–//– >] represent a recombination process. The right hand portion indicates the wavelengths (in nm) for the possible transitions. The last right hand portion shows the ones that contribute to DC electrical conductivity.

said to obey the same Arrhenius equation, i.e. we would have
$\sigma = \sigma \cdot \exp\{-(E_1 - E_2)/kT\}$.

And hence we have $(E_1 - E_2) = 1.7 - 1.4 = 0.3$ eV, which is the activation energy in the curve's second segment. With the ending of the holes, we have a pure contribution to the electric conductivity band and the activation energy is equal to 1.7 eV in the third segment. This explains the Fe(II) curve.

Let us apply the above idea to PPT itself. We have five segments:

1. Soliton's electron excitation + soliton's hole recombination: $1.7 - 1.7 = 0.0$ eV. The soliton's electron has to go to the conduction band so it can move freely and hence be captured by a hole. This region ends with complete exhaustion of the electrons of the soliton's state ($<$ 40°C).
2. Polaron's electron excitation $=$ 2.0 eV. This region begins with the next upper electrons, i.e. those of the polaron at 2.0 eV (40–60°C).
3. Polaron's electron excitation + excess of holes due to the adsorbed water release for which the activation energy is higher than E_1: i.e. $E_2 > E_1$, and we get a positive slope in the curve (60–70°C)!
4. Polaron's electron excitation + polaron's hole recombination: $2.0 - 1.4 = 0.6$ eV. The same idea here as in the first segment (70–120°C).
5. Valence band excitation: the intrinsic region $=$ 3.4 eV (120–140°C).

By this idea the whole behaviour of the compounds can be explained. This is shown in Fig. 7. Table 2 summarizes the calculations of the activation energies for the other complexes in the different temperature ranges.

It appears that the adsorbed water on its attachment to the polymer's main chain localizes the electron's wave function and hence decreases the electric conductivity. On the release of adsorbed water by heating, the quasi-particles (solitons

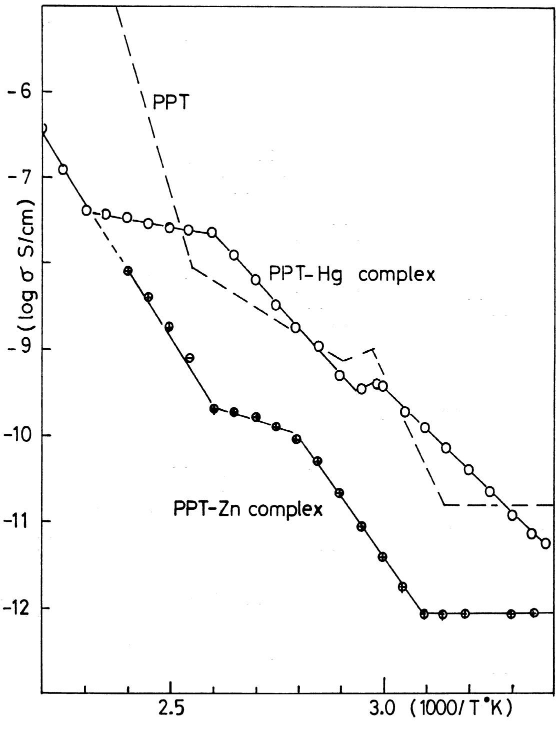

Fig. 8. A comparison between PPT-Zn complex and PPT-Hg complex.

Table 2
Calculations of the activation energies for the polymer's complexes

M	Range (T °C)	S°	H	E_a (eV)	M	Range (T °C)	S°	H	E_a (eV)
Mn	0–100	1.7	1.7	0.0	Ni	< 25	1.7	1.7	0.0
	100–140	1.7	0.0	1.7		25–85	1.7	0.95	0.75
	140–160	1.7	1.7	0.0		85–92	1.7	> 1.7	+ ve
	> 160	1.7	0.0	1.7		> 92	1.7	.75	0.95
Fe	< 30	1.7	1.7	0.0	Cu	< 50	1.7	0.85	0.85
	30–110	1.7	1.4	0.3		50–60	1.7	1.7	0.0
	110–170	1.7	0.0	1.7		60–72	1.7	0.85	0.85
	170–180	1.7	1.7	0.0		72–90	1.7	1.7	0.0
	> 180	1.7	0.0	1.7		90–120	1.7	0.85	0.85
Co	< 25	1.7	1.7	0.0	Zn	120–130	1.7	> 1.7	+ ve
	25–60	1.7	0.87	0.83		< 50	1.7	1.7	0.0
	60–110	1.7	0.3	1.4		50–85	1.7	0.3	1.4
	110–125	1.7	> 1.7	+ ve		85–110	1.7	1.4	0.3
	> 125	1.7	0.3	1.4		110–144	1.7	0.0	1.7

M = metal; S° = neutral soliton; H = hole of a polaron if it is less than 1.7 eV.

and polarons) will be released as explained above. This is accompanied with chain's relaxation and hence the exothermal phenomenon.

5.1.1. The 5d complex

A probing trial is carried out to compare the 3d-transition elements with those of the 5d-elements using mercury as an example. Fig. 8 shows both Zn and Hg complexes. Two features are clearly apparent. First, the behaviour of the Hg complex curve can be explained, including the positive activation energy kink, using the proposed energy band model; with solitons and polarons. The reader can try the same calculation with three polarons at 2.0, 2.5 and 2.7 eV. Second, the DC electrical conductivity below 130°C is higher in case of Hg than in case of the Zn complex. The contribution of the 5d-electrons to the number of the polymer's main chain electric carriers is higher than the case of 3d-electrons. The 5d-electrons are more shielded from the metallic nucleus than the 3d-ones. Above 130°C and with the depletion of the quasi particles; i.e. the solitons and polarons, the intrinsic character of complexes takes over, with activation energy equal to 1.7 eV for both elements.

6. Conclusion

The following five points can be concluded:

1. The complete behaviour of the DC electric conductivity curves for PPT and its complexes are explained via the energy band model. The energy gap of the bulk is about that of the molecule (3.4 eV). On the other hand, the complexes have half this value (1.7 eV).
2. The pairs of electrons on nitrogen and sulfur play some role (not a small one it appears) in the DC electrical conductivity. This is manifested in the low conductivity values of PPT with adsorbed water, or its complexes with or without adsorbed water. It appears that any factor, which localizes these electrons, will affect the free passage of the conjugated wave function along the chain. Hence, one gets a lower conductivity value.
3. This study shows the effect of adsorbed water on the DC electrical conductivity behaviour under temperature variations. As can be seen from the analyses, the water attaches itself to specific points on the chain. These points are not equivalent. The attachment will result in: (a) localization of the N (and/or) the S electron pairs mentioned above; and (b) the creation of the quantum quasi-particles, solitons and polarons. The release of this adsorbed water by temperature will result in the release of quasi-particles. Hence, with the increase of temperature, one gets the excitation of electrons from the soliton's level to the conduction band. These electrons will either contribute to the number of the conductivity carriers or recombine with the positive holes. The fast mechanism will decrease the number of the conductivity carriers. Also it may be the reason for the exothermal phenomenon observed. The higher the released number of adsorbed water molecules, the higher the number of conductivity carriers, and hence the higher the conductivity values. This appears in the case of Cu complexes.
4. Complexation with the 3d-transition elements will reduce the value of the DC electrical conductivity in one of the routes of conjugation (Scheme 1). Again there is a localization of the N and S electron pairs as in case of water, if not harder, hence, the lowering of DC electrical conductivity. Complexation may cancel, change the position, or create additional polarons. This can be attributed to an interaction between the 3d-electrons of the transition element and those of the π-bond, albeit via the nitrogen and sulfur electron pairs.
5. The 5d-element (Hg) complex with PPT follows almost

the same behaviour as the 3d-elements, The difference is in the lower temperature region where it has a higher DC electrical conductivity value. This has been attributed, in our opinion, to the shield effect of the 5d-electrons from the metallic nucleus and hence the higher contribution to the carriers' number. This needs further investigation, we hope to carry out in future.

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