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# Poly[di(2,5-dimercapto-1,3,4-thiadiazole)-metal] Complexes of Group IIB: Synthesis, Characterization and DC Electrical Conductivity

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The reaction of 2,5-dimercapto-1,3,4-thiadiazole (DMT) (6.6 mmol) with zinc, cadmium and mercury chlorides (3.3 mmol) gave new polymer-metal complexes. The poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-metal complexes of Zn(II), Cd(II) and Hg(II) were characterized by elemental analyses, electronic spectra, FTIR spectroscopy, thermal analyses (TGA and DTA) and X-Ray diffraction. The DC electrical conductivity variation with temperature in the range 300-500 K of the polymer-metal complexes after annealing for 24 h at 100°C and after doping with 5% $I_2$ is determined for comparison. The activation energies were calculated and the results were interpreted using the band energy model.

**Keywords:** Poly[di(2,5-dimercapto-1,3,4-thiadiazole)-metal] complexes, 2,5-dimercapto-1,3,4-thiadiazole, DC electrical conductivity, doping, thermal analysis, X-ray diffraction, activation energies

## 1 Introduction

2,5-Dimercapto-1,3,4-thiadiazole (DMT) and poly-DMT (PDMT) have attracted the attention of researchers due to their wide applications in many fields such as synthesis of novel heterocyclic compounds with antimicrobial activity, (1,2) advanced technology materials, determination of trace elements (3) and lithium secondary batteries (4,5). Successful commercial applications of electrically conducting polymers have triggered intensive research (6,7). Furthermore, much attention has been directed to polymeric metal complexes by researchers working in areas such as protective coatings, catalysts, semiconductors and analytical methods (8,9).

A new series of transition metal polymer complexes from DMT and the chlorides of Zn(II), Cd(II) and Hg(II) in the backbone of the chain was synthesized, characterized and described in this study. The presence of three transition metals in group IIB allowed the comparison of the chemical and physical properties: FTIR, UV-vis, thermal analyses (thermogravimetric analysis (TGA) and differential thermal analysis (DTA)) and DC electrical conductivity. The most important part of this work is the comparative study of the DC electrical conductivity. The DC electrical conductivity of the polymer-metal complexes was studied in the annealed and 5% $I_2$ doped states, with temperature variation in the range 300–500 K. The activation energies (Ea) were calculated from the DC electrical conductivity and thermal analyses.

## 2 Experimental

### 2.1 Chemicals

The chemicals, synthesized or purchased (Aldrich chemicals), were recrystallized twice before use. The solvents were reagent grade: 99% absolute ethanol, dimethylformamide (DMF) (BDH, AnalaR®).

### 2.2 Synthesis of the Polymer-Metal Complexes

A solution of the anhydrous metal chlorides of [(Zn(II), Hg(II)) and (Cd(II).$2H_2O$)] (3.3 mmol) in ethanol (25 mL) and water (5 mL) was added to a solution of 2,5-dimercapto-1,3,4-thiadiazole (6.6 mmol) in ethanol (25 mL). The mixture was refluxed with stirring using a magnetic bar for 24 h under a thin stream of nitrogen gas. The precipitated polymer was separated by filtration and then washed several times with hot ethanol and dried in the air for 24 h.

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### 2.3 Instrumentation

The melting points were measured on an electrothermal melting point apparatus. FTIR spectra were recorded using the KBr disc technique on a Shimadzu 8101 FTIR Spectrophotometer. The elemental (CHNS) analyses were performed on an elemental analyses system GmbH VARIOEL $V_{2.3}$ 1998 CHNS Mode. The UV and visible absorption spectra were measured in DMF using a PU 8800 UV-Visible Automatic Scanning Philips Spectrophotometer. The thermal analyses (TGA and DTA) were carried out on a Shimadzu TGA-50H and Shimadzu DTA-50 at 25 to 600°C under 20 mL nitrogen per minute and a heating rate of 10°C per minute. The X-Ray diffraction was carried out on a Bruker Axs Da Advance, Germany. The electrical conductivity measurements was measured on a Keithley Picoammeter/Voltage Source Model 6487. The doped polymer was prepared by mixing 5% (w/w) $I_2$ with 200 mg of the polymer, then ground well and pelleted into circular discs of 12.5-mm diameter and thickness of 0.8 to 1 mm under $10^4$ $\mathrm{Kgcm^{-1}}$ pressure in an IR dye. More details about doping and annealing were performed as described previously (10).

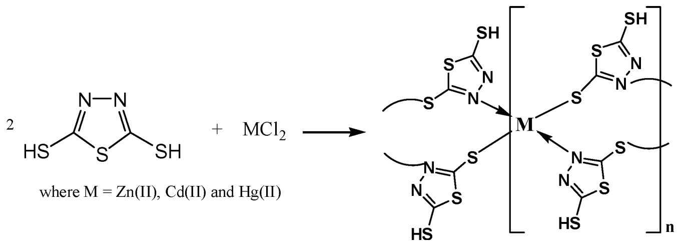
### 2.4 Thermal Analyses of the Poly[di(2,5-Dimercapto-1,3,4-thiadiazole)-metal] Complex

The thermogravimetric analysis (TGA) of the poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-metal complexes was investigated for the thermal decomposition behavior. The thermograms [TGA, derivative thermogravimetric (DTG) and (DTA) curves] were obtained. For each step in the decomposition sequence, the following parameters were determined: from DTG curves of decomposition, $T_i$ was taken as the point at which the DTG curve begins to deviate from its base line as initial reaction and the point at which the DTG curve returns to its base line, was taken as a final temperature of decomposition $T_f$. The temperature of maximum rate of weight loss $T_{DTG}$ is obtained from the intersection of tangents to the DTG peak. From the TGA curves, the weight loss at the decomposition step $\Delta$m is determined from the point $T_i$ up to the end of the reaction at the point $T_f$.

The activation energy $E_a$ was calculated from the slope of a plot of the Coats-Redfern equation (11) for the reaction order $n \neq 1$. The order of reaction n is determined by the Horovitz-Metzger method (12):

$$\mathrm{Ln}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \mathrm{Ln}\frac{ZR}{qE}\left[1-\frac{2RT}{E}\right] - \frac{E}{RT} \quad (1)$$

where: $\alpha$ = fraction of weight loss, T = temperature (K), n = order of reaction, Z = pre-exponential factor, R = molar gas constant, $E_a$ = activation energy and q = heating rate.



**Sch. 1.** Synthesis of the poly[di(2,5-dimercapto-1,3,4-thiadiazole)-metal complexes.

## 3 Results and Discussion

### 3.1 Synthesis and Characterization

The poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-metal complexes (Scheme 1) were prepared by the reaction of 2,5-dimercapto-1,3,4-thiadiazole (2 moles) with anhydrous zinc, mercury chlorides and the cadmium(II) chloride dihydrate (1 mole) in ethanol under reflux for 24 h, under a thin stream of nitrogen gas. Table 1 summarized the physical properties (color, % yield and CHNS) of the three polymer metal complexes.

All the polymer-metal complexes showed melting points above 275°C. The reaction yields ranged from 33 to 90%. The colors of the polymer complexes are different. The zinc complex is white and those of cadmium and mercury are light yellow.

### 3.2 FTIR Spectra

The main FTIR bands of the poly[di(2,5-dimercapto-1,3,4-thiadiazole)-metal] complexes are summarized in Table 2. The assigned absorption bands are consistent with the suggested structures.

The stretch $\nu$(S-H) weak band showed up weakly at 2491 $\mathrm{cm^{-1}}$ and the deformation antisymmetric $(\delta_{as})$ (C—SH) in-plane and deformation symmetric $(\delta_s)$ $(\text{C-SH})_{ip}$ were also weak bands at 948 $\mathrm{cm^{-1}}$ and 923 $\mathrm{cm^{-1}}$, respectively (13). All these bands showed up as very weak bands in the polymer-metal complexes. The noticeable shift in position of the $\nu_{as}$(C=N), $\nu_s$(C=N) and $\delta$ ring for the four polymer-metal complexes compared to DMT, is assurance of formation the polymer-metal complexes products (8).

The starting material DMT showed many bands and broadband absorptions in the range 3100–1800 $\mathrm{cm^{-1}}$. These bands are attributed to overtones and combinations, except two bands that appeared at 2519 and 2485 $\mathrm{cm^{-1}}$ corresponding to the $\nu_{as}$(S—H) and $\nu_s$(S—H), respectively. The broadening of these features might be due to the presence of extensive hydrogen bonding of SH groups (13,14).

**Table 1.** Characterization data of poly[di(2,5-dimercapto-1,3,4-thiadiazole-metal] complexes

| | | | *CHNS % calcd (found)* | | | |
|---|---|---|---|---|---|---|
| *Polymer-metal complexes* | *Formula (M.W)* | *Color (Yield %)* | *C* | *H* | *N* | *S* |
| **PDMT-Zn** | $C_4H_2N_4S_6Zn$<br>(363.87) | White<br>(33) | 13.20<br>(13.25) | 0.55<br>(0.45) | 15.40<br>(15.27) | 52.87<br>(56.38) |
| **PDMT-Cd** | $C_4H_2N_4S_6Cd.C_2H_5OH$<br>(454.94) | Light yellow<br>(76) | 15.84<br>(15.32) | 1.33<br>(1.15) | 12.32<br>(11.90) | 42.29<br>(42.46) |
| **PDMT-Hg** | $C_4H_2N_4S_6Hg$<br>(499.81) | Light yellow<br>(90) | 9.63<br>(9.66) | 0.40<br>(0.44) | 11.23<br>(11.26) | 38.55<br>(39.02) |

**Table 2.** Main FTIR bands of the poly[di(2,5-dimercapto-1,3,4-thiadiazole)-metal] complexes

| *Polymer-metal complexes* | *DMT cm$^{-1}$* | *PDMT –Zn cm$^{-1}$* | *PDMT-Cd.$C_2H_5OH$ cm$^{-1}$* | *PDMT-Hg cm$^{-1}$* |
|---|---|---|---|---|
| N(S—H) | 2491 w | 2491 vvw | 2491 vvw | 2491 vvw |
| $\nu_{as}$(C=N) | 1512 s | 1487 | 1482 | 1474 |
| $\nu_s$(C=N) | 1457, 1393 m | 1418 | 1427 | 1422 |
| Δ ring | 1273 s | 1307 | 1299 | 1277 |
| $\delta$ (CNNC)$_{ip}$ | 1128, 1098 w | 1106 | 1119, 1098 | 1110 |
| $\nu$(N—N) | 1085, 1055 m | 1046 | 1042 | 1046 |
| $\delta_{as}$ (C—SH)$_{ip}$ | 948 w | 948 vw | 931 vw | 960 vw |
| $\delta_s$ (C—SH)$_{ip}$ | 923 w | 923 vw | – | 925 vw |
| $\nu_{as}$(C—S) | 756,722 s | 743 | 730 | 730 |
| $\nu_s$(C—S) | 662 vw | 675 | 640 | 670 |
| $\nu_{as}$(C—S') | 585 w | 589 | 580 | 585 |
| $\nu_s$(C—S') | 542 vw | 551 | 546, 533 | 555,534 |

v, very; w, weak; $\nu$, stretch; $\delta$, deformation; s, symmetric; as, antisymmetric; ip, in-plane, bend.; bending.

### 3.3 Electronic Spectra

The main UV-visible absorptions of poly[di(2,5-dimercapto-1,3,4-thiadiazole)-metal] complexes are shown in Table 3.

All the polymer-metal complexes showed two or three $\pi$-$\pi^*$ (K-band) $\lambda_{max}$ at 200–270 nm and another two n-$\pi^*$ (R-band) at $\lambda_{max}$ 335–465 nm characterized as ligand-to-metal charge transfer. The charge transfer transition band showed up in the visible region for each of the three polymer-metal complexes namely, PDMT-Zn at 465 nm, PDMT-Cd and PDMT-Hg at 470 nm each. This proves the metal complexation and that the bands are due to L → M (15,16).

### 3.4 Thermal Analysis

The DC electrical conductivities of the polymer-metal complexes were studied in the temperature range (300–500 K;

**Table 3.** Main UV-visible absorptions of poly[di(2,5-dimercapto-1,3,4-thiadiazole)-metal] complexes

| | $\pi$-$\pi^*$ | | | n-$\pi^*$ | | |
|---|---|---|---|---|---|---|
| *Polymer-metal Complexes* | $\nu_{max}$ nm | $\nu_{max}$ (cm$^{-1}$) | $E_a$(eV) | $\nu_{max}$ nm | $\nu_{max}$ (cm$^{-1}$) | $E_a$(eV) |
| DMT | 220 | 45500 | 5.6 | 355 | 28200 | 3.5 |
| | 230 | 43500 | 5.4 | | | |
| | 270 | 37040 | 4.6 | | | |
| PDMT-Zn | 200 | 50000 | 6.2 | 335 | 28200 | 3.5 |
| | 220 | 45500 | 5.6 | 465 | 21500 | 2.7 |
| | 270 | 37040 | 4.6 | | | |
| PDMT-Cd.$C_2H_5OH$ | 270 | 37040 | 4.6 | 350 | 28600 | 3.5 |
| | | | | 470 | 21700 | 2.6 |
| PDMT-Hg | 200 | 50000 | 6.2 | 335 | 28200 | 3.5 |
| | 230 | 43500 | 5.4 | 470 | 21700 | 2.6 |
| | 250 | 40000 | 5.0 | | | |

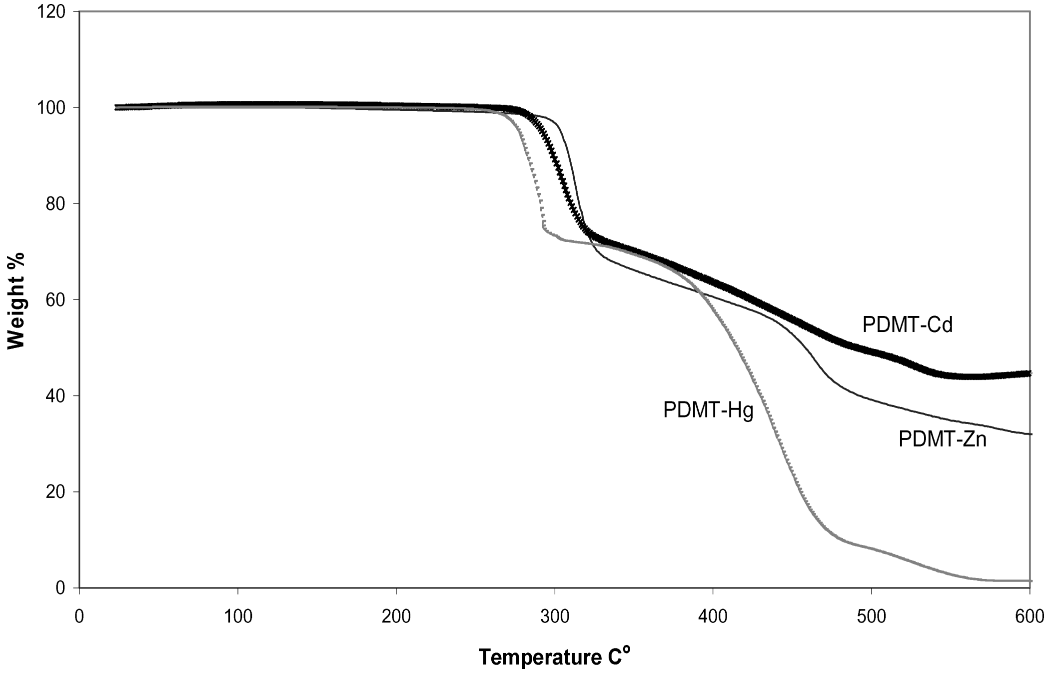


**Fig. 1.** TGA curves of the poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-metal complexes.

25–225°C). Hence, we will concentrate on the same range in studying the thermal analyses.

The difference in the thermal decomposition behavior of the three poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-metal complexes under a nitrogen atmosphere can be seen clearly in their (TGA) and (DTA) curves (Figures 1 and 2). For each step in the decomposition sequence, it was possible to determine the following thermal parameters; $T_i$, $T_f$, $T_{DTG}$, $\Delta$m and $E_a$ which are summarized in Table 4. The samples of the polymer-metal complexes were annealed before analyses hence EtOH did not show up in TGA of PDMT-Hg.[17] The three polymer-metal complexes are thermally stable at 300 to 500 K.

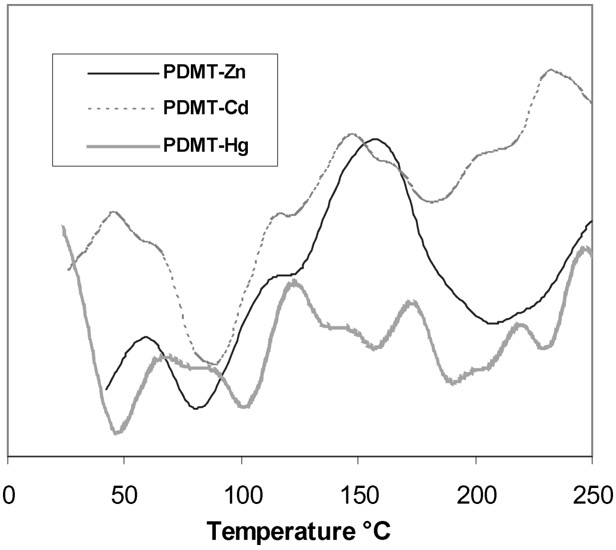


**Fig. 2.** DTA curves of the poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-metal complexes.

### 3.5 X-Ray Diffraction Patterns

The most direct method of investigation of the structure of the polymer (crystalline and amorphous) is the X-ray diffraction analyses (18). The X-ray diffractographs of the poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-metal complexes were studied in the $2\theta = 10°–80°$ region at room temperature. All the X-ray diffractographs indicated crystalline structures for the three polymer-metal complexes.

From the XRD patterns observed, the degree of crystallinity was based on the total intensity of the diffraction peaks of these polymer-metal complexes (19). They follow the order PDMT-Cd > PDMT-Hg > PDMT-Zn.

### 3.6 DC Electrical Conductivity

The DC electrical conductivity of the polymer-metal complexes was measured vs. 1000/T in the range 300–500 K. The effect of the annealing and the acceptor doping with 5% $I_2$ of the three polymer-metal complexes after annealing upon conductivity is measured for comparison. The DC electrical conductivity of the annealed and doped poly[di(2,5-dimercapto-1,3,4-thiadiazole)-metal] complexes are summarized in Table 5. The polymer-metal complexes responded to heat by an increase in the electrical conductivity and behaved almost similarly; this is a typical behavior of semiconductor materials

**Table 4.** Thermal gravimetric data of poly[di(2,5-dimercapto-1,3,4-thiadiazole-metal] complexes

| | | *TGA* | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *Polymer-metal complexes* | *Step* | *Wt Loss % Found (Calc.)* | $T_i/^\circ C$ | $T_f/^\circ C$ | $T_{DrTGA}$ | *Res. % f(Calc.)* | *Ea kJmol$^{-1}$ (Ea eV)* | *React* |
| PDMT-Zn | 1st | 33.76<br>(33.95) | 244 | 356 | 319 | 64.99<br>(66.05) | 224.8<br>(2.33) | 41.5% bb |
| | 2nd | 31.14<br>(31.76) | 427 | 504 | 470 | 33.85<br>(34.26) | 217.1<br>(2.25) | 38.9% bb |
| PDMT-Cd | 1st | 44.37<br>(44.62) | 270 | 345 | 315 | 53.03<br>(55.38) | 58.36<br>(0.60) | 55.24% bb |
| | 2nd | 41.06<br>(40.00) | 345 | 590 | 510 | 14.58<br>(15.38) | 80.40<br>(0.83) | 54.21% bb |
| PDMT-Hg | 1st | 27.87<br>(27.61) | 246 | 330 | 301 | 72.13<br>(72.39) | 68.66<br>(0.712) | 46.59% bb |
| | 2nd | 63.99<br>(63.34) | 330 | 508 | 456 | 8.14<br>(9.05) | 81.48<br>(0.844) | Hg + 39.79 % bb |
| | 3rd | 6.73<br>(6.6) | 508 | 591 | 540 | 01.41<br>(2.45) | 91.18<br>(0.945) | 11.25 % bb |

bb, backbone.

(20,21). All annealed and doped polymer-metal complexes showed three stages or steps which means, each one has three activation energies, except PDMT-Zn which displayed two stages only and hence two activation energies. Most of the breaks maybe attributed to phase transitions (physical changes); this is confirmed by the small peak in the same range in the DTA that does not correspond to weight loss in the TGA curve (22). Therefore, we will try to follow the relation between the DTA peaks and the breaks on the DC electrical conductivity of only the annealed polymer-metal complexes.

Figure 3 shows the behavior of the electrical conductivity vs. 1000/T in the range 300–500 K for the annealed polymer-metal complexes. All the annealed and doped polymer-metal complexes showed DC electrical conductivity of $10^{-14}$–$10^{-13}$ Scm$^{-1}$at ambient temperature except the doped PDMT-Zn which started at $2.6 \times 10^{-11}$S cm$^{-1}$. They all showed an increase in the DC electrical conductivity by heat. The highest DC electrical conductivity of the annealed PDMT-Zn is at ambient and higher temperatures. The lowest DC electrical conductivity was for the annealed PDMT-Hg at ambient and high temperatures.

The DC electrical conductivity vs. 1000/T of the 5% $I_2$ doped poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-metal complexes are displayed in Figure 4. The highest DC electrical conductivity at ambient temperature was noticed for the doped PDMT-Zn, while the highest DC electrical conductivity at higher temperature was noticed for the doped PDMT-Hg. The annealed and doped PDMT-Cd is in the middle at ambient and higher temperatures. It is obvious that the annealed polymer-metal complexes did not respond to doping and gave the same DC electrical conductivity at 300 K. The internal doping of the polymers by the metals present in their backbones causes this (23).

Figure 5 shows the DC electrical conductivity vs. 1000/T of the annealed and doped poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-Zn(II) complex. The highest DC electrical conductivity at ambient and higher temperatures was noticed for doped PDMT-Zn and the increase started at ambient temperature in the annealed state, while the doped state start the enhancement at about 112°C. The annealed and doped PDMT-Zn gave a DC electrical conductivity of $5.8 \times 10^{-13}$ and $2.6 \times 10^{-11}$ S cm$^{-1}$ at ambient temperature and $1.6 \times 10^{-12}$ and $2.2 \times 10^{-8}$ S cm$^{-1}$ at 225°C, respectively. The breaks at 112 ± 4°C in the DC electrical curve for both states, maybe assigned to phase transition, which does not correspond to weight loss in the TGA curve, whereas the 112 ± 4°C in the DTA curve was between endothermic and exothermic peaks.

**Table 5.** DC electrical conductivity of the annealed and doped poly[di(2,5-dimercapto-1,3,4-thiadiazole)-metal] complexes

| | *Annealed (100°C/24 h) S cm$^{-1}$* | | *Doped/annealed (5% $I_2$) S cm$^{-1}$* | |
|---|---|---|---|---|
| *Polymer-metal complex* | *300 K* | *500 K* | *300 K* | *500 K* |
| PDMT-Zn | $5.8 \times 10^{-13}$ | $1.6 \times 10^{-8}$ | $2.6 \times 10^{-11}$ | $2.2 \times 10^{-8}$ |
| PDMT-Cd.$C_2H_5OH$ | $2.8 \times 10^{-13}$ | $8.6 \times 10^{-9}$ | $8.4 \times 10^{-14}$ | $7.0 \times 10^{-7}$ |
| PDMT-Hg | $3.5 \times 10^{-14}$ | $1.0 \times 10^{-9}$ | $7.4 \times 10^{-14}$ | $1.4 \times 10^{-6}$ |

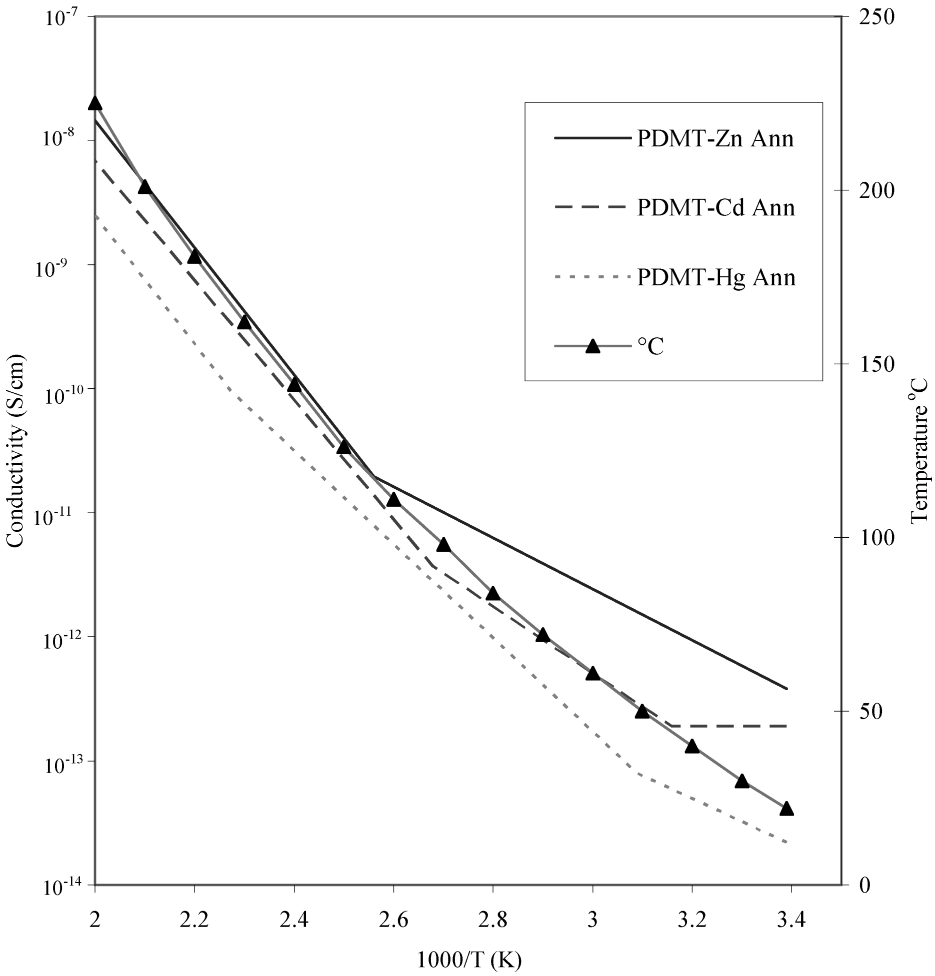


**Fig. 3.** DC electrical conductivity vs. 1000/T of the annealed poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-metal complexes.

Usually the doped materials give higher conductivities, however, these materials have metals in their backbone and the salts of these metals, like $ZnCl_2$ are known to be good dopants. Thus, these materials are doped internally (24), and the external doping will not enhance the DC electrically conductivity that much.

Figure 6 shows the DC electrical conductivity vs. 1000/T of the annealed and 5% $I_2$doped poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-Cd(II) complex. The highest DC electrical conductivity at ambient temperature is noticed for the annealed PDMT-Cd. This is not in accordance with the normal case. However, the highest DC electrical conductivity at higher temperature is noticed for the doped PDMT-Cd, this is usually the doped materials act. Also, the enhancement of DC electrical conductivity did not start at ambient temperature in the two cases. The annealed and doped PDMT-Cd gave a DC electrical conductivity of $8.6 \times 10^{-8}$ and $7.0 \times 10^{-7}$ $Scm^{-1}$ at high temperature, respectively. The annealed PDMT-Cd have two breaks at 40°C and 70°C, these degrees of temperature are clearly shown on DTA, especially at 70°C is the starting point of the main endothermic peak.

Figure 7 shows the DC electrical conductivity vs. 1000/T of the annealed and doped poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-Hg(II) complex. The highest DC electrical conductivity at ambient and higher temperatures is noticed for doped PDMT-Hg and the enhancement started at ambient temperature for the annealed and doped states. The annealed and doped PDMT-Hg gave a DC electrical conductivity of $3.5 \times 10^{-14}$ and$7.4 \times 10^{-14}$ $Scm^{-1}$ at ambient temperature and $1.0 \times 10^{-9}$ and $1.4 \times 10^{-6}$ $Scm^{-1}$ at 500 K, respectively. The breaks for annealed state at 50°C in the DC electrical conductivity curve maybe attributed to phase transition. This is confirmed by the appearance of endothermic peak at about the same range in the DTA, which does not show a weight loss in the TGA curve.

### 3.7 Activation Energies

Table 6 summarizes the calculations for the bulk activation energies (Ea) at different temperature ranges for all the segments of the curves of the annealed and doped polymer complexes. The carriers available for the DC electrical conductivity are electrons and holes. The three

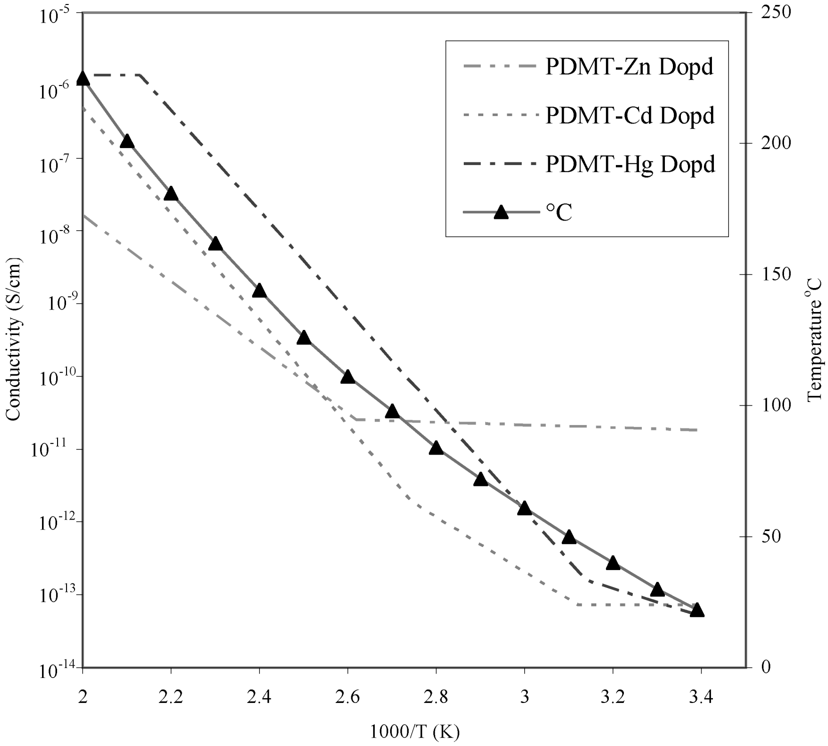


**Fig. 4.** DC electrical conductivity vs. 1000/T of the doped (5% $I_2$) poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-metal complexes.

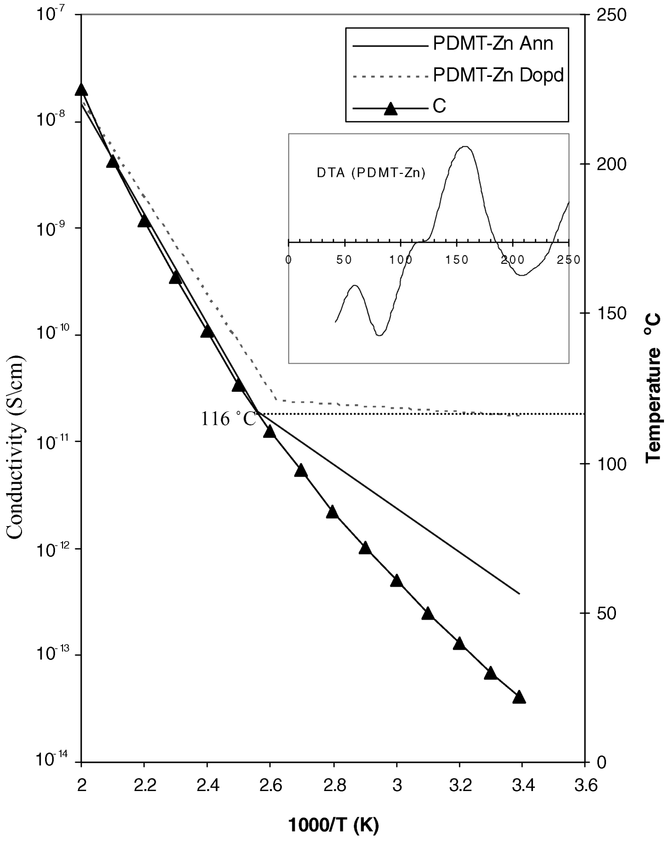


**Fig. 5.** DC electrical conductivity vs. 1000/T of the annealed and doped (5% $I_2$) poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-Zn(II) complex.

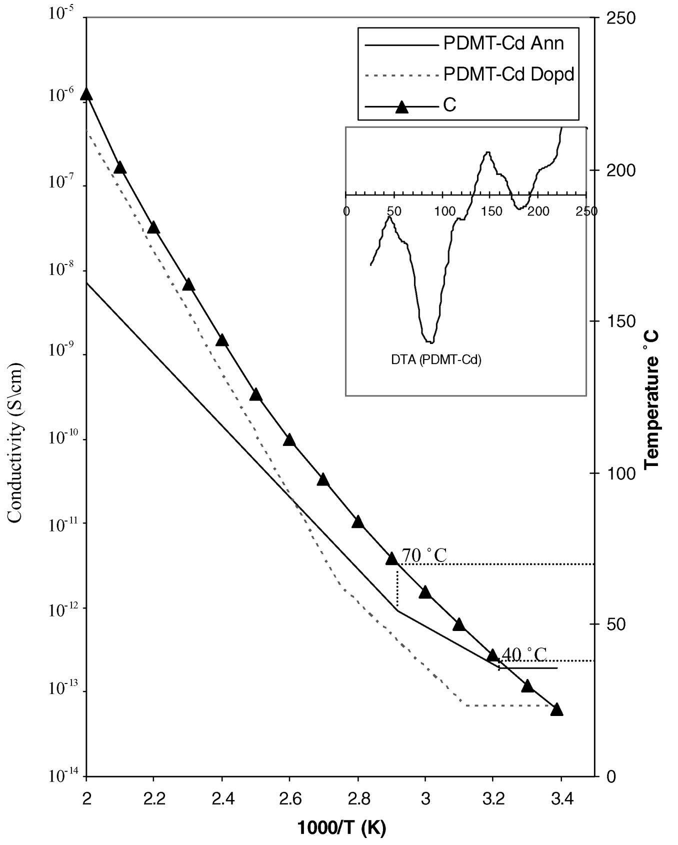


**Fig. 6.** DC electrical conductivity vs. 1000/T of the annealed and doped (5% $I_2$) poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-Cd(II) complex.

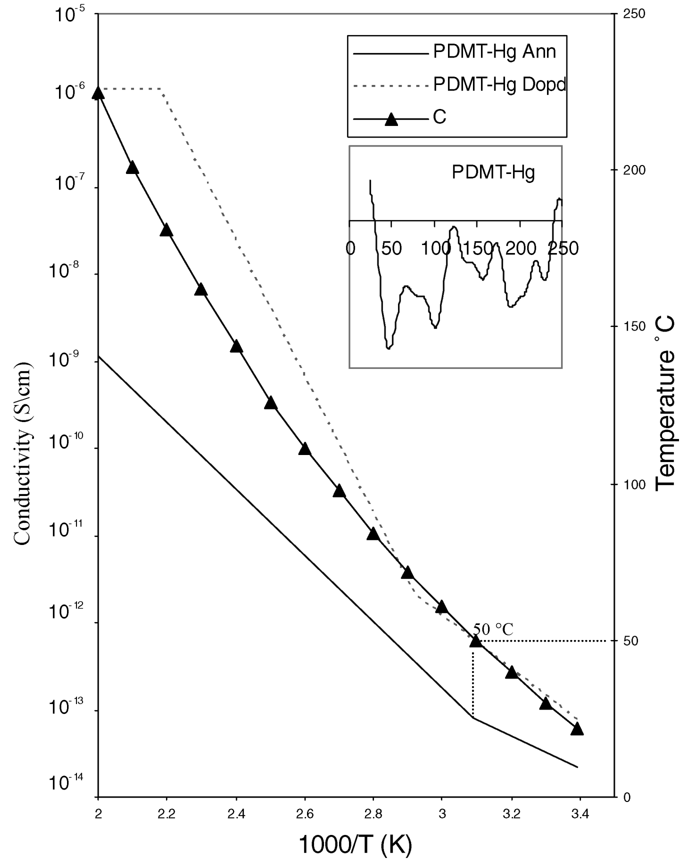


**Fig. 7.** DC electrical conductivity vs. 1000/T of the annealed and doped (5% $I_2$) poly[di(2,5-dimercapto-1,3,4-thiadiazole)]-Hg(II) complex.

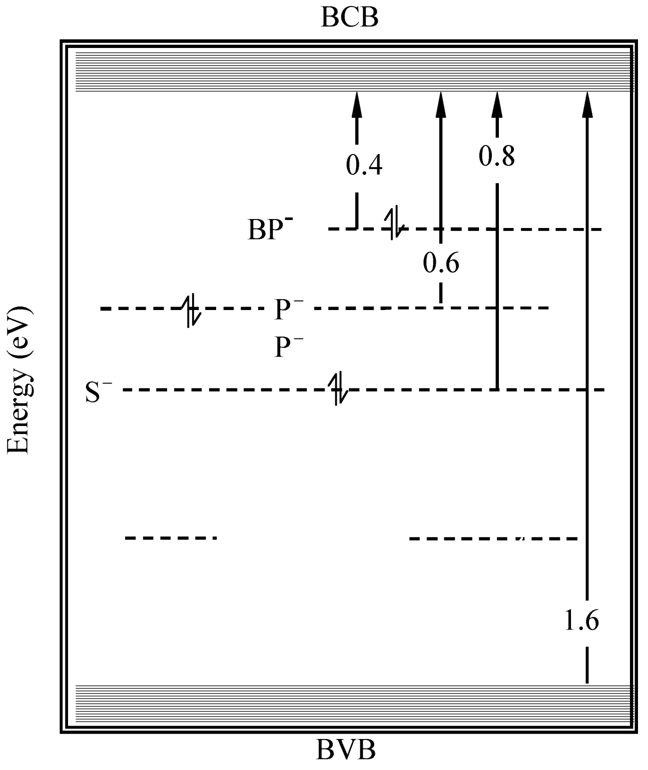


**Fig. 8.** Proposed energy schematic model based on the band theory of the polymer-metal complexes.

polymer-metal complexes (Zn, Cd and Hg) showed two to three segments and activation energies each. These segments are due to physical changes (phase transitions or chain conformation) as confirmed by DTA. To explain the Figures 3–7, of DC electrical conductivity vs. 1000/T of the annealed and doped PDMT-M's, Figure 8 is introduced, which presents an energy schematic model based on the band theory. In our case, the bulk energy gap (BEG) is about 1.6 eV. This is the highest activation energy obtained.

For the annealed PDMT-Zn, the first segment is due to the excitation from the upper level of the carriers of the negative bipolaron ($BP^-$), which is 0.4 eV. The second segment is due to a soliton level excitation (i.e., in the middle of (BEG) (25) which is about 0.8 eV. For the doped state, the first segment is due to recombination or annihilation (R), which is 0.0 eV. The second segment is due to a soliton ($S^-$) level excitation, which is a about 0.8 eV.

**Table 6.** Calculations for the bulk activation energies (Ea) at different temperature ranges of annealed and doped polymer-metal complexes

| | *Annealed (100° C/24 h)* | | | *Doped (5% $I_2$)* | | |
|---|---|---|---|---|---|---|
| *Polymer-metal Complex* | *T(° C)* | *Ea eV* | | *T(° C)* | *Ea eV* | |
| PDMT-Zn | 25–115 | 0.4 | BP- | 25–108 | 0.0 | R |
| | 115–225 | 0.8 | S | 108–225 | 0.8 | S |
| PDMT-Cd | 25–40 | 0.0 | R | 25–40 | 0.0 | R |
| | 40–100 | 0.4 | BP- | 40–90 | 0.8 | S |
| | 100–225 | 0.8 | S | 90–225 | 1.6 | VB |
| PDMT-Hg | 25–50 | 0.4 | BP- | 25–45 | 0.6 | P- |
| | 50–225 | 0.8 | S | 45–196 | 1.6 | VB |
| | | | | 196–225 | 0.0 | R |

R = recombination and annihilation, VB=valence band, W=water release, S=soliton, BP=bipolaron.

For the annealed PDMT-Cd, the first segment is due to the recombination and annihilation (R), which is 0.0 eV. The second segment is due to the excitation from the upper levels of the ($BP^-$), which is ~0.4 eV. The third segment is due to a soliton ($S^-$) level excitation, which is about 0.8 eV. In the doped state, the first segment is due to the recombination and annihilation (R), which is 0.0 eV. The second segment is due to a soliton ($S^-$), which is about 0.8 eV. Finally, the third segment is due to the excitation from the bulk valance band (BVB), which is ~1.6 eV.

For the annealed PDMT-Hg, the first segment is due to the excitation from the upper level of the carriers of the ($BP^-$), which is ~0.4 eV. The second segment is due to a soliton ($S^-$) level excitation, which is a about 0.8 eV. In the doped state, the first segment is due to the excitation from the upper level of negative polaron ($P^-$), which is ~0.6 eV. The second segment is due to the excitation from the bulk valance band (BVB), which is ~1.6 eV. The third segment is due to the recombination and annihilation (R), which is 0.0 eV.

## 4 CONCLUSIONS

The following points can be concluded from this work:

1. Reaction of the 2,5-dimercapto-1,3,4-thiadiazole with metal chlorides formed polymer-metal complexes of the type $[ML_2]_n$. Their physical properties such as TGA, DTA, X-ray diffraction and DC electrical conductivity are studied.
2. The polymer-metal complexes are thermally stable at 300 to 500 K.
3. The electrical conductivity of the polymer-metal complexes, whether annealed or doped, increased with increasing temperature due to the variation of the carrier concentration with temperature as in the case of semiconductors.
4. The polymer-metal complexes have metals in their backbones and the salts of these metals are known to be good dopants. Thus, these materials are internally doped, so the doped polymer-metal complexes are only one or two orders of magnitude higher in DC electrical conductivity than the annealed state.
5. The three polymer-metal complexes (Zn, Cd and Hg) showed two to three segments and activation energies each due to physical changes (phase transitions or chain conformation) as confirmed by DTA.

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