DC Electrical Conductivity of Polyazomethinethiosemicarbazone Metal Complexes

Ali El-Shekeil, Fatma Al-Yusufy, Abdul-Hafeedh A. Abdulla

Department of Chemistry, Faculty of Science, Sana'a University, Sana'a, Yemen

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ABSTRACT: Polyazomethinethiosemicarbazone (PATS) metal complexes of Ni(II), Co(II), Cu(II), Zn(II), Cd(II) and Hg(II) metal ions were prepared by reacting the polymer ligand (PATS) with the appropriate metal salt in refluxing DMSO. Elemental analyzes as well as FTIR and electronic spectral data are presented to confirm the formulation of the isolated materials. The spectral data show that the ligand polymer is bonded to the metal ions via the thiol sulfur atom and coordinated through the nitrogen of azomethine group. The DC electrical conductivity measurements of PATS and its metal complexes were measured in the range 300–500 K in the annealed and 5% iodine doped forms. The products gave electrical conductivity in the semiconducting region that increased by heat. The DC electrical conductivity is interpreted using the band gap theory using solitons, polarons and bipolarons. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1538–1544, 2010

Key words: polyazomethinethiosemicarbazone metal complexes; DC electrical conductivity; doping; electronic spectra; and activation energies

INTRODUCTION

Forty years ago, all carbon-based polymers were strictly regarded as insulators. The notion that plastics could be made to conduct electricity would have been considered to be absurd. Indeed, plastics have been extensively utilized by the electronics industry for this property. Since the discovery of organic conducting polymers, intensive research has been made with the aim of designing polymers with good conducting properties[1,2] Doping polyazomethines with iodine have been reported to raise the electrical conductivity which is originally in the order 10^{-12}–10^{-10} S cm^{-1} to 10^{-7}–10^{-4} S cm^{-1}.[3–5]

Polyazomethinethiosemicarbazone (PATS) is considered a hybrid between Schiff bases and thiosemicarbazones. These polymers and their metal complexes show considerable interest for various reasons. The presence of donor atoms such as N and S in the polymer backbone contributes greatly to the thermal and environmental stability and enhances electrical conductivity. Other important features are the nature of metal-sulfur bonding interaction and their biological activity.[6,7]

To study the structure-property correlation, we extended this work to synthesize a polymer containing alternative sequences of thiosemicarbazone and phenylene residues linked together by azomethine moieties. Presence of azomethine moieties in the polymer backbone has shown to be useful in preparing materials with good thermal and physico–mechanical properties.[8]

A polymer containing [—CH=N—NHC=S—] moiety, rich in electrons, is synthesized to enhance electrical conductivity along the chains.[9] This polymer is also considered as a suitable ligand, which is expected to form stable chelates with 3d transition metals.[10] PATS metal complexes of Ni(II), Co(II), Cu(II), Zn(II), Cd(II), and Hg(II) metal ions were prepared by reacting the polymer ligand (PATS) with the appropriate metal salt in refluxing DMSO.

Metal complexation is a great way for chemical modification of these polymers. Such materials exhibit a wide variety of interesting electronic and optoelectronic properties. Complexation may lead to metal cross-linking which is expected to enhance intermolecular interactions and consequently promotes electrical conductivity.[11,12]

As a continuation of our interest in conducting polymers,[13–15] the objective of this study is: (i) to synthesize the PATS, (ii) To shed some light on the DC electrical conductivity of the pure and doped polymers, (iii) to investigate the ability of the polymer ligand to form metal-chelates with metals under study, (iv) to study the structure-property relationship of the polymer and its metal complexes.

EXPERIMENTAL

Chemicals

Chemicals (Aldrich) were subjected to purification before use. Terephthaldehyde was recrystallized

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Correspondence to: A. El-Shekeil (shekeil2000@yahoo.com).

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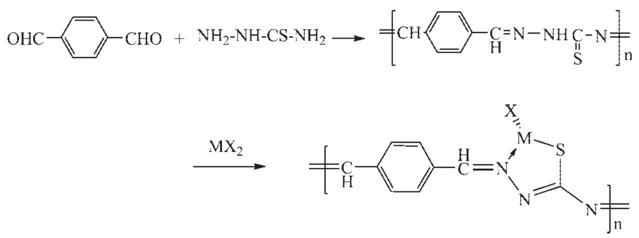

Scheme 1 Preparation of polymer ligand and the polymer complexes.

from a 10% methanol/90% water mixture. Thiosemicarbazide was recrystallized from water. The solvents used were reagent grade. DMF (BDH) (Analar), absolute ethanol and methanol (Fluka) were used as supplied.

Synthesis of the polymer ligand (PATS)

PATS is synthesized as reported previously.[9]

Chemical complexation

The polymer metal complexes of Co(II), Ni(II), Cu(II) Zn(II) Cd(II), and Hg(II) were chemically prepared. A typical procedure is as follows:

A mixture of the polymer (1.89 g, 10 mmol) in 25 mL DMSO and cobalt acetate tetrahydrate (2.38 g, 10 mmol) in 15 mL DMSO was stirred at 100°C under a thin stream of nitrogen for 24 h. The reaction mixture was poured dropwise into 500 mL distilled water with continuous stirring. A dark powder-like precipitate of the polymer complex was filtered by suction in a Buchner funnel, washed thoroughly three times with hot distilled water and dried in oven at 100°C for 2 h.

Physical measurements

The melting points were measured in degrees Celsius, on a digital electro-thermal melting point apparatus. The FTIR spectra were recorded using the KBr disc technique on a JASCO 410 FTIR Spectrophotometer. The elemental (CHNS) analyzes were performed using an Exeter CE-440 Elemental Analyzer. The UV and visible absorption spectra were measured in DMSO ($\sim 10^{-5}$ mol/dm^3) using a Pye Unicam 8800 UV-Visible Automatic Scanning Spectrophotometer. The thermal analysis is carried out on STA 625.

The electrical conductivity measurements

The electrical conduction measurements, annealing and doping were performed as described previously.[16,17]

RESULTS AND DISCUSSION

The polymer ligand was prepared according to Scheme 1. Thiosemicarbazone was reacted with terephthaldehyde to give PATS. The polymer complexes were prepared by heating PATS with the appropriate metal salts in DMSO for 24 h. The synthesis method is a convenient and simple route to a variety of amine and thiol groups and transition metal complexes.

The physical data of the polymer ligand and polymer metal complexes are summarized in Table I. The results of the elemental analyzes are in good agreement with the calculated values. The polymer is partially soluble in DMSO. The polymer metal complexes were found to be stable with high melting points (>350°C) and insoluble in all common organic solvents attempted. This precluded their characterizations by suitable techniques like viscometry, NMR and conductance. The electronic spectra were measured in DMSO in which the polymer complexes were partially soluble.

From the elemental analyzes the nickel PATS complex was found to make one complexation for every two units, however, the cadmium PATS complex was found to make a complexation every six repeating units. This is reflected in the yields too. The Cd PATS complex showed the lowest yield (61%) among them due to its inability to react followed by the nickel PATS complex (80%). All other PATS metal complexes took a metal per repeating unit.

TABLE I
The Physical Properties of Chemical Complexes of PATS

Product (formula)	Repeat unit wt.	Color	Yield (%)	CHNM (%) calculated (found) C	 H	 N	 M
PATS ($C_9H_7N_3S$)	189	Yellow	96	57.10 (57.40)	3.70 (4.12)	22.20 (21.20)	–
PATS-Co ($C_9H_6N_3S$-Co) H_2O.Oac	323.9	Black	98	40.75 (42.35)	3.75 (3.70)	12.97 (11.95)	22.75 (23.56)
PATS-Ni ($C_{18}H_{12}N_6S_2$-Ni) Cl	435	Beige	80	49.66 (48.35)	2.76 (3.04)	19.31 (19.24)	13.33 (12.60)
PATS-Cu ($C_9H_6N_3S$-Cu) 0.5H_2O.OAc	319.5	Light brown	89	41.25 (42.37)	3.44 (3.58)	13.15 (13.30)	24.38 (25.40)
PATS-Zn ($C_9H_6N_3S$-Zn).Cl	253	Pale yellow	87	42.69 (43.86)	2.37 (4.40)	16.60 (16.00)	25.69 (24.99)
PATS-Cd ($C_{54}H_{36}N_{18}S_6$-Cd) Cl	1240	Dark yellow	61	52.26 (53.63)	2.90 (3.10)	20.32 (19.91)	9.03 (8.40)
PATS-Hg ($C_9H_6N_3S$-Hg).Oac	389	Dark brown	90	29.53 (30.33)	2.46 (2.50)	9.39 (8.87)	44.74 (45.00)

TABLE II
The Main FTIR Absorption Bands and Assignments for PATS and its Metal Complexes

Polymer	C-Har.	C=C, C=N	C—H_{ip}	C—H_{00p}	C—N	H_2O
PATS	3128	1560, 1638	1013	845, 783	1282	3423, 950
PATS-Co	3055	1560, 1638	1013	781,738	1281	3449, 950
PATS-Ni	3080	1543, 1609	1013	845,781,738	1281	3423, 930
PATS-Cu	3173	1543, 1609	1027	843,781,738	1274	3424, 950
PATS-Zn	3080	1561, 1618	1025	843	1280	3423, 951
PATS-Cd	3030	1546, 1608	1013	846,781,738	1283	3425, 951
PATS-Hg	3168	1455, 1609	1015	849,776,742	1285	3418, 950

The glass temperature of PATS metal complexes was computed from DSC and was in the range 301–398°C.

PATS may be represented by the two tautomeric forms[9] i.e., the thione and/or thiol form. However, the thiol group was never detected in the polymer ligand or complexes; the thiol group shows up as a weak band at 2550 cm^{-1} in the FTIR.

IR spectra

The main IR absorption bands of polymer and polymer metal complexes are summarized in Table II. There are some similarities in the finger print region.[18] The absorption bands appeared to satisfy the suggested structures. The bands at 1608–1638 cm^{-1} may be assigned to the C=C and C=N stretch in the polymer and its metal complexes. The aromatic C—H stretch bands are seen at 3030–3173 cm^{-1}. PATS itself and all its metal complexes exhibited a broad absorption band at 3400–3450 cm^{-1} regions assigned to ν(OH) and $\sigma(H_2O)$, which is indicative for the coordinated and combined water.

Electronic spectra

The main resulting electronic absorptions are summarized in Table III. All the materials showed one π–π^* (K-band) or n-π^* (R-band) λ_{max} at 270–300 nm and another at λ_{max} 380–410 nm characterized as ligand-to-metal charge transfer,[19] besides a shoulder of d–d transitions in the visible region at 540–610 nm.

The electrical conductivity

The electrical conductivity behavior of annealed PATS and its metal complexes vs. 1000/T K^{-1} is shown in Figure 1. As a general feature, complexation enhanced conductivity of the polymer metal complexes which is higher than that of PATS itself. That is the complexation of PATS increased the DC electrical conductivity. Also the polymer ligand didn't respond to heat by increasing electrical conductivity until 120°C. However, the polymer metal complexes responded to heat by an increase in electrical conductivity starting from ambient temperature.

The polymer complexes behaved in a similar way. The curves of Cu, Ni, and Cd complexes showed three segments each, while Hg and Zn showed only two each; however Co gave only one temperature independent segment. A temperature independent segment is seen in case of the polymer ligand followed by another segment.

The electrical conductivity behavior of the materials after doping with 5% I_2 vs. 1000/T K^{-1} is shown in Figure 2. All doped materials showed higher conductivity than PATS except Ni. The same trend of the electrical conductivity was noted. All metal complexes showed three segments each except Cu and Co complexes which gave one segment each and Ni that showed two segments. The Co complex did not

TABLE III
The Main Electronic Absorptions of PATS and Complexes

	λ_{max} nm (cm^{-1}) eV		
Complex	π–π^* + n-π^*	M-L ch. tr.	Visible d–d transitions
PATS	300 (33,300) 4.13	390s (25,600) 3.18	600s (16,600) 2.07
PATS-Co	280 (35,700) 4.43	410s (24,400) 3.02	610s (16,400) 2.03
PATS-Ni	280 (35,700) 4.43	380s (26,300) 3.26	570s (17,500) 2.18
PATS-Cu	270 (37,000) 4.59	395 (25,300) 3.14	550s (18,200) 2.25
PATS-Zn	290 (34,500) 4.28	380 (26,300) 3.26	540s (18,500) 2.30
PATS-Cd	295 (33,900) 4.20	380s (26,300) 3.26	560s (17,900) 2.21
PATS-Hg	290 (34,500) 4.28	380s (26,300) 3.26	590s (17,000) 2.10

s, shoulder.

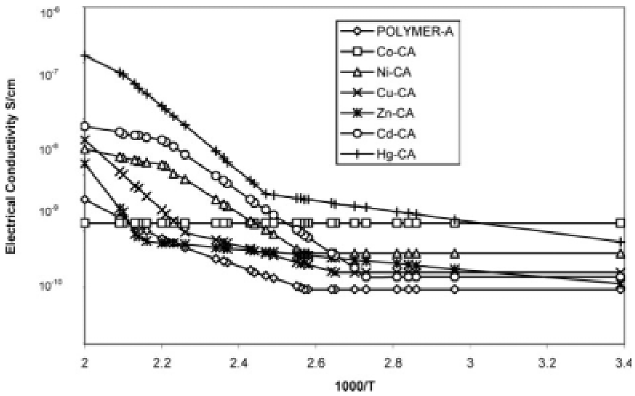

Figure 1 The DC electrical conductivity of the chemically synthesized annealed PATS metal complexes.

respond to heat at all and gave the same fairly high electrical conductivity at all temperatures. The doped PATS showed three segments.

Table IV summarized the increase in DC electrical conductivity by heat at 300–500°K for the PATS metal complexes in their annealed and doped forms. The electrical conductivity behavior of the annealed and doped polymer ligand vs. 1000/T K^{-1} is shown in Figure 3. Doping enhanced the electrical conductivity of PATS.

The 3d PATS complexes

The four 3d transition metals used in the chemical complexation are Co, Ni, Cu, and Zn. The behavior of the four 3d PATS metal complexes in the doped and annealed states are illustrated in Figures 4–7. From these figures a comparison can be made between annealed and doped PATS metal complexes. A few general features can be noted from the figures:

a. Doping increased the overall electrical conductivity.

b. The same activation energy values are found in some segments of the figures e.g. (0.94) is noticed in case of Ni, Cu, Zn, Cd, and Hg.

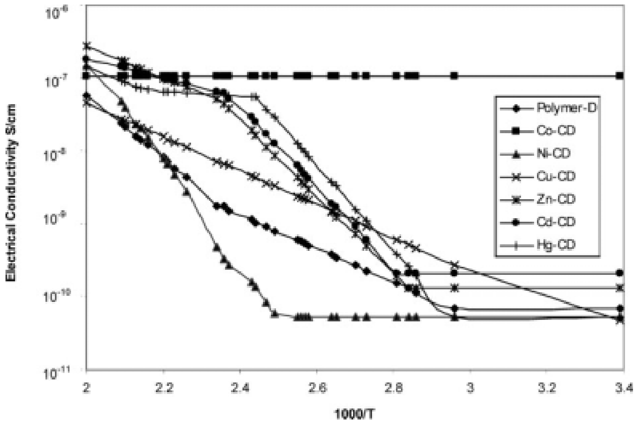

Figure 2 The DC electrical conductivity of the chemically synthesized doped PATS metal complexes.

TABLE IV
The Electrical Conductivities of the Chemically Synthesized PATS Metal Complexes in their Doped and Annealed Forms at 300°K and 500°K

	Annealed		Doped	
	300°K	500°K	300°K	500°K
PATS	4.9×10^{-11}	3.1×10^{-9}	4.2×10^{-11}	3.8×10^{-8}
PATS-Co	8.0×10^{-8}	8.0×10^{-8}	8.0×10^{-8}	8.0×10^{-8}
PATS-Ni	3.1×10^{-11}	2.6×10^{-9}	3.6×10^{-11}	4.4×10^{-8}
PATS-Cu	1.4×10^{-10}	3.6×10^{-8}	4.1×10^{-11}	3.7×10^{-8}
PATS-Zn	4.0×10^{-10}	4.0×10^{-8}	6.0×10^{-10}	2.1×10^{-7}
PATS-Cd	1.0×10^{-10}	4.4×10^{-8}	1.6×10^{-10}	1.6×10^{-7}
PATS-Hg	4.0×10^{-10}	3.2×10^{-7}	3.6×10^{-11}	4.5×10^{-8}

From the four figures, the activation energies of the annealed and doped complexes, number of segments, temperature ranges and assignments are summarized in Table V. The annealed materials were heated at 100°C for 24 hours; hence the presence of water was excluded. The doped polymer complexes showed the presence of water as seen in the FTIR by a broad band at 3400–3450 cm^{-1} (Table II), and elemental analyzes (Table I).

From Figure 4, the activation energy of the annealed and doped PATS cobalt complex showed one temperature independent segment each with a value of 0.00 eV.

Figure 5 shows two segments for the annealed PATS-Ni complex: 0.17 (<137°C), 0.90 (>137°C). The doped Ni complex showed two segments too: 0.26 (<160°C) and 0.94 eV (>160 °C).

Figure 6 shows three segments for the annealed polymer copper complex: 0.00 (<103°C), 0.36 (103–157°C) and 0.94eV (>157). The doped copper material showed only one segment: 0.45 (22–225°C).

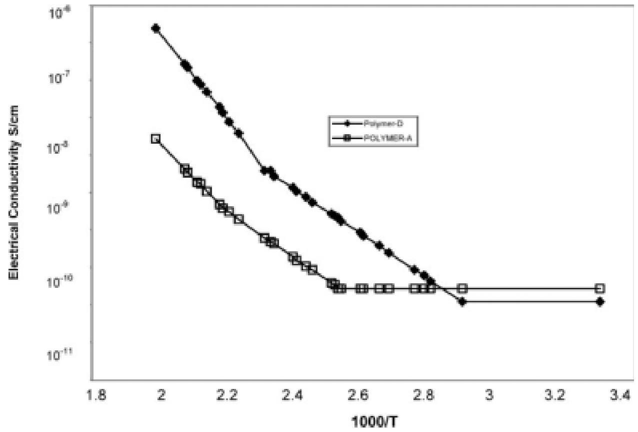

Figure 3 The DC electrical conductivity of the chemically synthesized doped PATS.

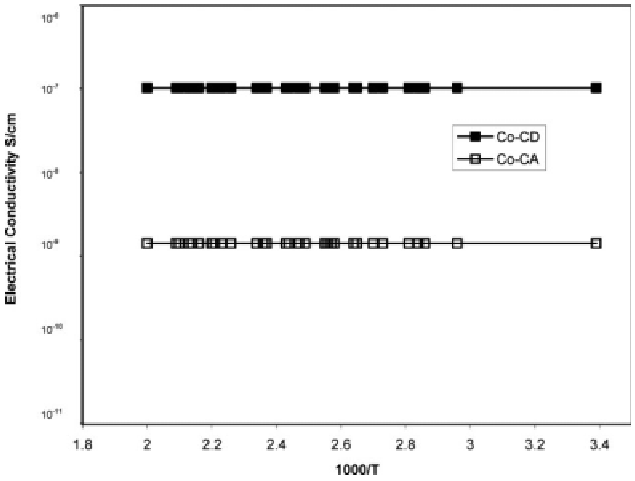

Figure 4 The DC electrical conductivity of the chemically synthesized annealed and doped cobalt polymer.

The polymer zinc complex (Fig. 7) showed two segments in its annealed state: 0.00 (<191°C) and 0.94 (>191°C). The doped material showed three segments with activation energies of 0.00 (<72), 0.94 (72–160), and 0.39 (>160).

The 4d PATS complex

Cadmium is selected in purpose as a 4d metal complex to compare with 3d transition metal complexes. The DC electrical conductivity of the annealed and doped cadmium complex is illustrated in Figure 8. The annealed form showed three segments: 0.00 (<95°C), 0.90 (95–152°C), and 0.49 (>152). The doped material showed three segments too with activation energy of 0.00 (<82), 0.94 (82–150°C), and 0.26 (>150°C).

The 4d-electrons are more shielded from the metallic nucleus than the 3d-electrons. The contribution of the 4d-electrons to the number of the main chain electronic carriers is higher in case of annealed and doped materials (see Figs. 1 and 2).

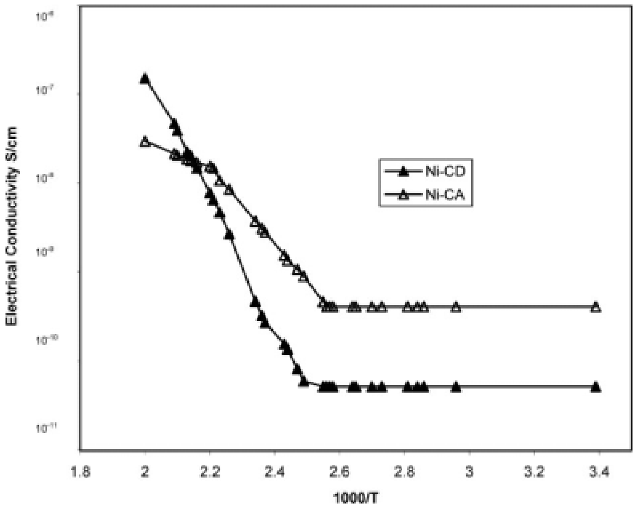

Figure 5 The DC electrical conductivity of the chemically synthesized annealed and doped PATS nickel complex.

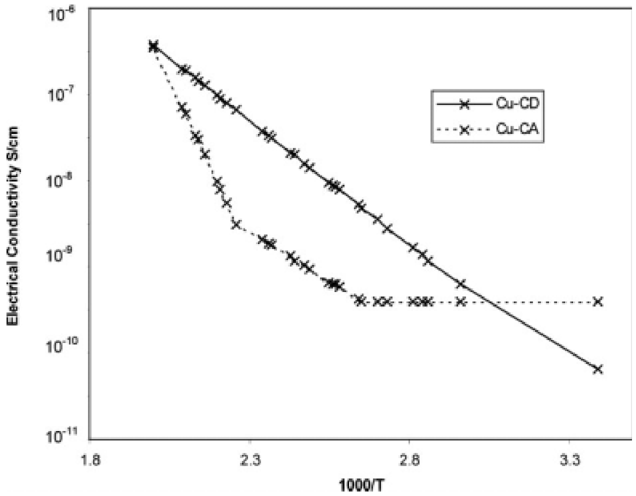

Figure 6 The DC electrical conductivity of the chemically synthesized annealed and doped PATS copper complex.

The 5d PATS complex

Mercury was selected as a probing trial to compare to the 3d and 4d transition metal complexes. Figure 9 shows the electrical conductivity vs. 1000/T K^{-1} of PATS mercury complex. The annealed form showed two segments: 0.17 (<129°C) and 0.94 (>129°C). The doped material showed three segments with activation energy of 0.00 (64°C), 0.94 (64–137°C) and 0.17 eV (>137).

The DC electrical conductivity was higher in case of polymer mercury complex, in the annealed state, than the 3d and 4d metal complexes. The contribution of the 5d-electrons to the number of the main

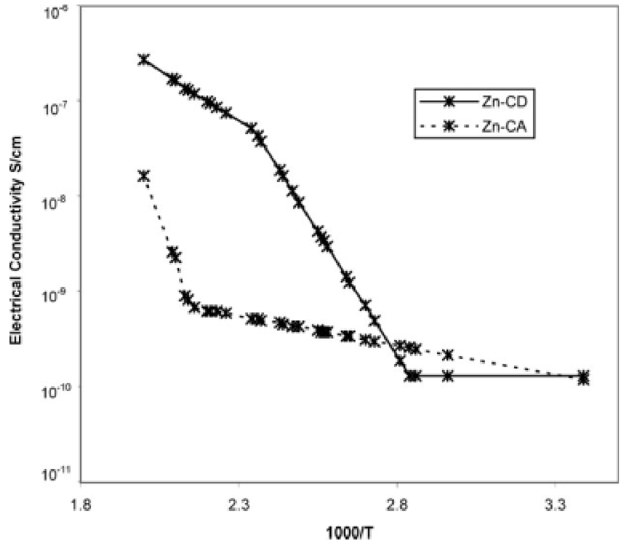

Figure 7 The DC electrical conductivity of the chemically synthesized annealed and doped zinc polymer.

TABLE V
Calculations of the Activation Energies for PATS and its Metal Complexes

	Annealed			Doped		
M	T (°C)	E_a (eV)		T (°C)	E_a (eV)	
PATS	22–116	0	ann.	22–64	0	ann.
	116–225	0.47	s	64–152	0.45	s
				152–225	0.79	BP−
Co	22–225	0	ann.	22–225	0	ann.
Ni	22–137	0.17	BP+	22–160	0.26	P+
	137–225	0.90	vb	160–225	0.94	vb
Cu	22–103	0	ann.	22–225	0.45	s
	103–157	0.36	S			
	157–225	0.94	vb			
Zn	22–191	0.66	P-	22–72	0	ann.
	191–225	0.94	vb	72–160	0.94	vb
				160–225	0.39	s
Cd	22–95	0	ann.	22–82	0	ann.
	95–152	0.90	vb	82–150	0.94	vb
	152–225	0.49	s	150–225	0.26	P+
Hg	22–129	0.17	BP+	22–64	0	ann.
	129–225	0.94	vb	64–137	0.94	vb
				137–191	0.17	BP+

chain electric carriers was higher in case of mercury. The 5p-electrons are more shielded from the metallic nucleus than the 3d and 4d-electrons (see Figs. 1 and 2 for comparison).

Activation energies

Table V summarizes the activation energies for all the segments of the curves of the annealed and doped polymer complexes. Figures 1 and 2 would be explained using Figure 10, which represents an energy schematic model based on the band theory for the annealed and doped polymer metal complexes. It covers the whole temperature variation for the DC electrical conductivity.

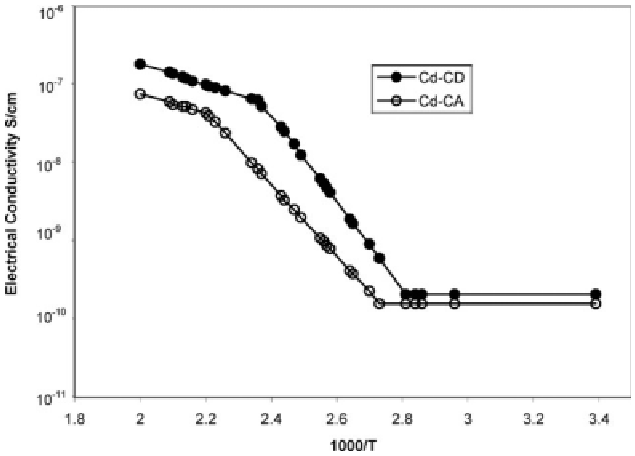

Figure 8 The DC electrical conductivity of the chemically synthesized annealed and doped PATS cadmium complex.

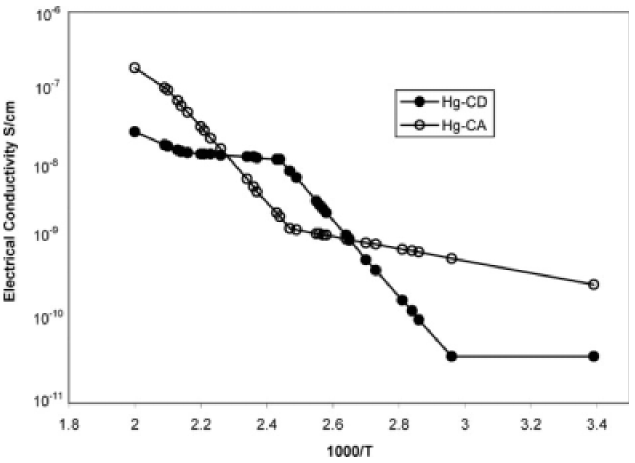

Figure 9 The DC electrical conductivity of the chemically synthesized annealed and doped PATS mercury complex.

The carriers available for the DC electrical conductivity are electrons and holes.[20,1] The electrons would be released from solitons, polarons or bipolarons. Using Arrhenius equation: $\sigma = \sigma^o \exp(E_1 - E_2/kT)$, all activation energies could be explained.

When the creation and combination of carriers are equal, one gets a temperature independent segment with E_a equals 0.00, i.e., $E_1 = E_2$, this is seen in PATS, annealed and doped, annealed complexes of Co, Cu, Cd and in doped complexes of Co, Zn, Cd, and Hg. This is caused by annihilation or recombination of carriers and holes.

Let us start by explaining the behavior of Figure 3 of the annealed metal complexes. The second

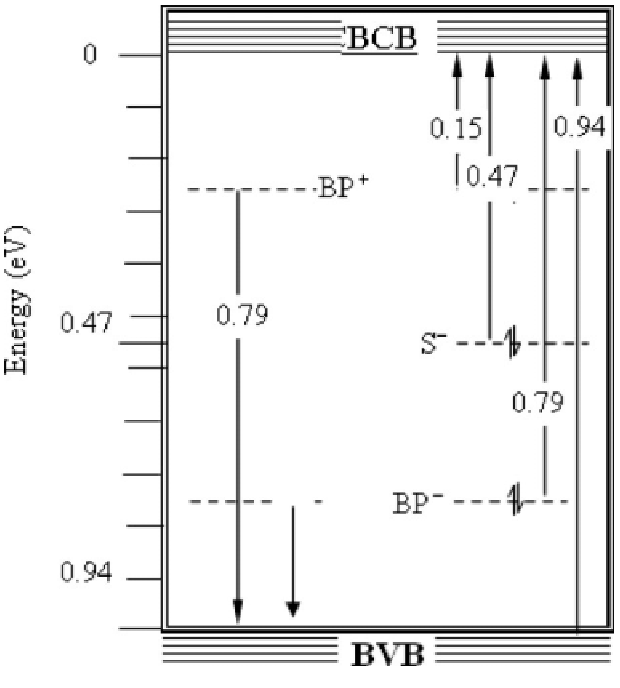

Figure 10 A schematic diagram for the activation energies of the annealed and doped PATS metal complexes.

segment of annealed PATS is 0.47 eV. This is half the value 0.94 noted in many annealed and doped complexes (Table V). By definition, this is the middle of the band gap which equals the energy gap of a soliton. Thus a soliton would give this value or less in case it faces a smaller hole. Almost the same value (0.49) is seen in case of Cd complex in the third segment which is a soliton. This is noted also in the second segment of Cu complex which equals 0.36 eV (<0.47). It combined with a smaller hole of 0.11 eV (0.47–0.36 = 0.11).

The first segment of the Cu complex gives activation energy of 0.17 eV. This is due to the excitation of a positive bipolaron (BP^+), which is ~ 0.17 eV below bulk conduction band (BCB). It is also noticed in the first band of PATS Hg complex.

A milestone in this work is the value 0.94 (or 0.90) noted in the second segment in case of Ni, Zn, Cd, and Hg and the third segment of Cu complex. This is attributed to the excitation of carriers from the bulk valence band (BVB) to the BCB.

The first segment in case of Zn complex gave a value of 0.66 eV. This is attributed to a negative polaron (P^-).

The behavior of the doped metal complexes illustrated in Figure 2 can be explained similarly. The activation energy of 0.45 eV seen in the second segment of PATS is caused by the release of a soliton. The same value is seen in case of Cu complex (0.45) and the third segment of Zn complex (0.39 eV). As stated previously, a soliton is less than or equal to 0.47 eV.

The third segment of doped PTA is attributed to the release of a negative bipolaron. By definition, a negative bipolaron equals the band gap minus a positive bipolaron (0.94–0.17 = 77) which is ~ 0.79 eV. Also a positive bipolaron equals the band gap minus a negative bipolaron (0.94–0.79 = 0.15) which is ~ 0.17 eV noticed in the third segment of Hg complex.[20] A positive polaron is noticed at 0.26 eV. This is calculated from the band gap minus the negative bipolaron (0.94–0.66 = 0.28) which is found to be ~ 0.26. All the activation energies can be clearly seen in Figure 10.

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