Spectroscopic Studies and Effect of Heat Treatment on Electrical Conductivity of New Diamino-Dicyano Thiophene Complexes

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Summary: The preparation and characterization of the 2,4-diamino- 3,5-dicyanothiophene complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and UO_2^{2+} acetates have been reported. The proposed structure was found to be 1:2 (LM_2) adducts of the ligand to the metal ion respectively which is supported by elemental analysis and magnetic measurements. Additionally mid-infrared and electronic absorption spectroscopic techniques, DTA, X-ray diffraction patterns have been reported. Moreover, the electrical conductivity of some selected complexes were measured before and after heat treatment above the transition temperatures.

Introduction

The heterocyclic compounds are important for their electrical properties and their applications as homogeneous catalysis[1-3]. The vibrational spectra of cyano-, and amino- complexes have been extensively studied[3-5]. The major impetus of the current study was focused on the novel 1,3-dicyano-2,4-diaminothiophene complexes which contain both cyano and amino groups. X-ray, IR spectra, magnetic properties, molar ratios and tentative vibrational assignment were used for elucidating the structure of these complexes. The electrical conductivity (EC) measurements have not been reported before for the investigated complexes. The present work deals with the effect of structure, complexation and heat treatment on electrical properties of some of these complexes.

Results and Discussion:

The recorded infrared (Fig. 1) and UV (Fig. 2) spectra as well as the x-ray diffraction patterns of some selected complexes confirm the complex formation, where (TGA) ensures the absence of coordinated water and the presence of water outside the coordinated sphere. DTA of some selected complexes confirms the loss of crystalline water due to changes observed around 100 °C. An additional peak recorded over 350°C confirms a phase transition which supported by electric conductivity measurements. The prepared complexes are paramagnetic except for the Pb^{2+} and Zn^{2+} which

means a weak field ligand in consistent with the effective dipole moment, μ_{eff} = 6.06 Debye obtained for nickel (II) complex. The later results approves four unpaired electrons in favor of $2M^{2+}$:1L ratio, see the following figures (the structure of the uranyl complex is illustrated separately).
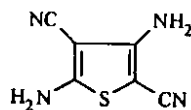
I
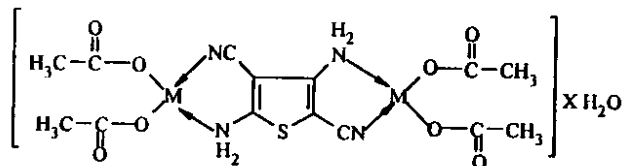
II(a-f)

a, M = Mn^{2+} X = 4	d, M = Cu^{2+} X = 1
b, M = Co^{2+} X = 4	e, M = Zn^{2+} X = 2
c, M = Ni^{2+} X = 4	f, M = Pb^{2+} X = 2

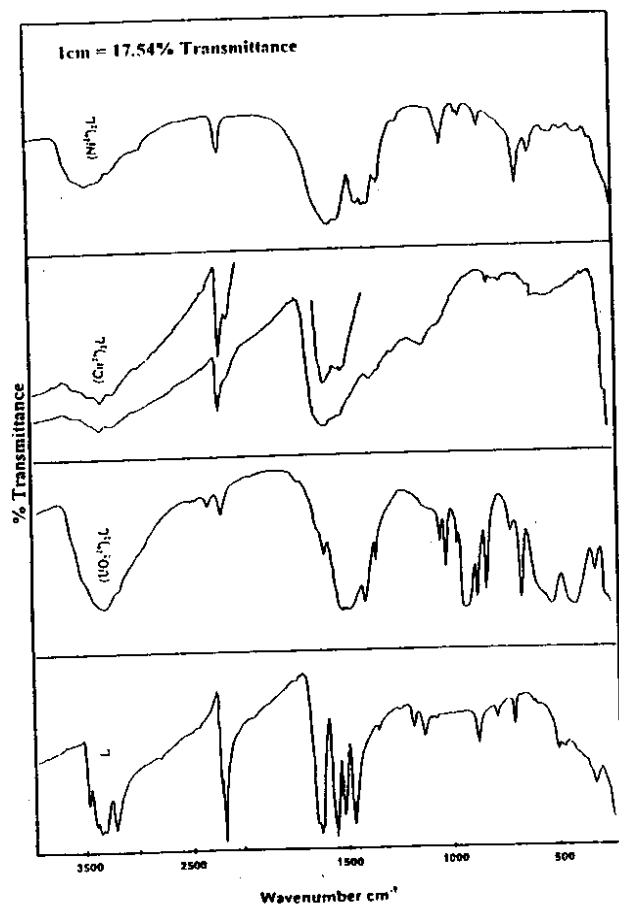where x is the number of water of crystallization

II g,   X = 2

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Fig. 1   The mid-infrared spectra (4000 - 400 cm^{-1})
of the solid complexes.
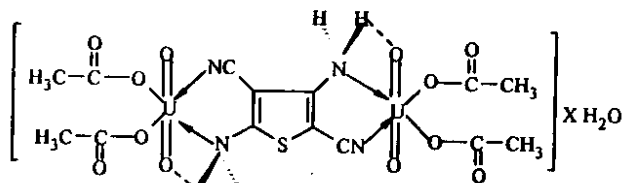
Fig. 2   The UV spectra in the visible region (200-
400 nm) of the solid complexes.

(1)Vibrational Spectral Data :

The vibrational spectra of cyano- and nitrile-complexes have been extensively studied [4,5]. Cyano complexes could be identified easily[8], since they exhibit sharp ν CN band(s) in the region of 2200-2000 cm^{-1}. The uncoordinated CN stretching vibration (2256-2245 cm^{-1}) tends to be shifted towards high frequencies (lower wavenumbers), upon coordination of the CN group with the divalent metal ion [9,10]. Also, the expected broadening in the region of NH$_2$ stretching vibrational modes for the complexes compared to relatively sharp bands of the uncoordinated amino group. The obtained complexes in the present investigation should spectroscopically exhibit the nature of both amino- and nitrile-complexes due to the use of 1,3-dicyano-2,4-diaminothiophene as a ligand which includes cyano and amino groups.
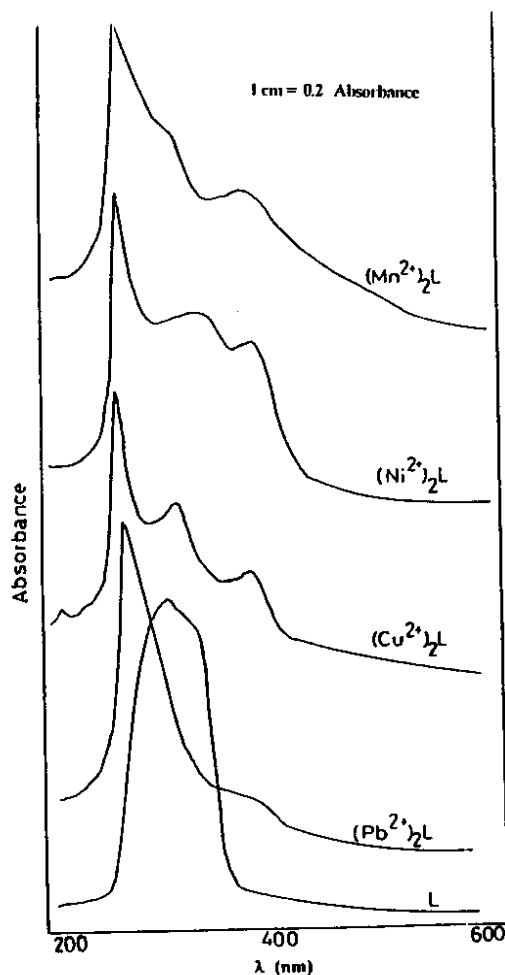
i) –NH$_2$ and –C≡N vibrational modes:

Firstly, we are focused on the infrared spectrum of the ligand, and comparing some of the fundamentals with that of the complex compounds. On the mid-infrared spectrum of the ligand, the observed bands at 3466 and 3375 cm^{-1} along with the 3401 and 3316 cm^{-1} bands, could be assigned to ν$_s$ NH$_2$ and ν$_{as}$ NH$_2$, respectively due to the approximate 70 cm^{-1} separations between the NH$_2$ symmetric and antisymmetric stretches[10]. The additional band recorded at 3214 cm^{-1} goes for the stretching mode of the hydroxyl group (moisture traces of the KBr pellets not from the prepared ligand) [9]. The obvious broadening of the stretching vibrational modes of the NH$_2$ group (3200-3400) which was observed in mid-infrared spectra of the

Table 1. Elemental analysis of some 2,4-diamino- 3,5-dicaynothiophene complexes.

Comp. No.	Color	Yield %	Molecular formula	M.Wt	Elemental Analyses Calculated/Found				
					C %	H %	N%	S%	M%
I	gray	85	$C_6H_4N_4S$	164.00	43.9	2.5	34.1	19.5	—
					43.7	2.3	33.7	19.2	
IIa	brown	70	$C_{14}H_{24}N_4O_{12}SMn_2$	582.3	28.9	4.2	9.6	5.5	18.8
					28.6	4.1	9.9	5.7	18.5
IIb	br.red.	60	$C_{14}H_{24}N_4O_{12}SCo_2$	590.3	28.5	4.1	9.5	5.4	19.9
					28.7	4.4	9.9	5.6	19.7
IIc	deep br.	70	$C_{14}H_{24}N_4O_{12}SNi_2$	589.8	28.5	4.1	9.5	5.4	19.9
					28.2	4.0	9.4	5.7	19.6
IId	green	80	$C_{14}H_{18}N_4O_9SCu_2$	545.5	30.8	3.3	10.3	5.9	23.3
					30.6	3.5	10.1	5.6	23.4
IIe	pale white	45	$C_{14}H_{20}N_4O_{10}SZn_2$	567.2	29.6	3.6	9.9	5.6	23.1
					29.3	3.8	9.7	5.4	23.4
IIf	black	55	$C_{14}H_{20}N_4O_{10}SPb_2$	850.8	19.8	2.4	6.6	3.8	48.7
					19.6	2.3	6.3	3.5	48.3
IIg	yellowish	80	$C_{14}H_{20}N_4O_{14}SU_2$	976.5	17.2	2.1	5.7	3.3	—
					17.3	2.4	5.9	3.1	

Table 2. Infrared spectral analysis of some 2,4-diamino- 3,5-dicaynothiophene complexes.

Comp. No.	IR			Tentative assignments			UV
	$\nu_{as} NH_2$	$\nu_s NH_2$	$\nu_{as} C≡N$	$\nu_s C≡N$	ν OCO	ν M–N	λ max
I	3466	3375	2213	2182	———	—	309.9, 336.1
IIa	3330	3209	2204	——	1574 & 1556	543	265.6, 314.8, 396.8
IIb	3337	—	2200	——	1568	394	265.7, 330.4, 395.3
IIc	3429(v.br)	——	——	2179	1569 & 1531	387	265.6, 344.3, 394.9
IId	3328 (v.br)	—	2198	——	1574 & 1553	394	262.3,331.4,387
IIe	3400 (v.br)	—	2197	—	1577	421	266.1, 387.2
IIf	3328 (v.br)	—	2205	——	1574 & 1556	265	265.o, 386.7
IIg	3294 (v.br)	——	2189	——	1514 & 1503	259	266.7, 337.1, 398.9

complexes under investigation (Fig. 1) provide us with a clear evidence that the divalent ions undergo complexing with the ligand. Furthermore, the observed fundamentals for the complex compounds are shifted towards lower wavenumbers compared with the same vibration for the ligand, which confirms the formation of the coordinated bond between the metal and the NH_2 and CN groups (M–N) bond, see Table 2. The same interpretation could be applied for the CN stretching modes in the region of 2100-2300 cm^{-1}. For the infrared spectrum of the ligand, two sharp and strong bands were observed at 2213 and 2182 cm^{-1} have been assigned to the antisymmetric and symmetric stretches of the CN groups, respectively. It should be mentioned that, because of the .observed broadening upon complexation, only the antisymmetric stretching vibrations was observed in the infrared spectrum for the CN and NH_2 groups.

For the infrared spectrum of the ligand, only three bands were observed below 600 cm^{-1} at 500, 469 and 317 cm^{-1}, where no bands were recorded for

the acetate group[10] in the region of 600-400 cm^{-1}. Thus, the additional bands measured within the same region should be interpreted for the fundamentals of the complex. The M–N stretches are reported in Table (2) in agreement with those reported earlier[11-15].

The recorded UV spectra confirms the complex formation, due to the lack of resemblance between the UV spectrum of the free ligand and the UV spectra of the prepared complexes. Furthermore, the spectrum of the ligand is characterized by a very broad absorption peak, λ_{max}. at 309.9 nm with a shoulder at 336.1 nm, however three absorption bands are observed in the corresponding spectra of the complexes except for the Zn^{2+} and the Pb^{2+} which having paired electrons. The additional band should be assigned to the d-d transitions. All the IR and UV results are summarized in Table (2). Additionally, The x-ray data shows the diffraction pattern of UO_2 (II) (DADCT) complex is completely different than those of the other complexes. the degree of crystallinity of UO_2 (II) complex more

obvious, while the other metal ion complexes tend to be more amorphous.

(ii) Electric Conductivity:

The conductivity measurements have been recorded over a temperature range of 25 - 400 °C applying the following equation[16],

$$\sigma = \sigma^\circ \, exp \, (-E/2kT) \qquad (1)$$

where σ is specific conductivity at absolute temperature T, σ° is a constant, k is Boltzmann constant and E is the energy gap (E_g). The relation between the logarithm of electrical conductivity before and after heat treatment (Run I and Run II) versus the reciprocal of absolute temperature illustrated in (Fig. 3a and 3b). The energy gaps for the samples (Fig. 4) before and after heat treatment (E_1 and E_2 respectively) have been determined from the linear parts after knee temperature (Fig. 3). Energy gaps, conductivities and ionic radii have been reported in Tables (3&4).

The complexity of DADCT (2,4-diamino-3,5-dicyanothiophene) with different divalent metal ions allows possible formation of several approximately separated electronic systems. The phase transition phenomenon have been observed for the ligand and for all complexes, where an irreversible phases appeared for some complexes at transition temperature. The observed phase transition may be attributed to a change in the type of packing which leads to a change in the single - triplet separation energy[17] This change can be seen from the relatively high activation energy of conduction obtained above transition temperature ($E_g = 2E^*$)). The relatively lower value of E_2 compared with E_1 (except for ligand) indicates the existence of permanent phases having an increase in the electrical conductivity. The DTA measurements indicate phase transitions in all complexes, where knee temperature values obtained from conductivity measurements (Fig. 3) are in agreement with those obtained from DTA analysis.

In view of the general assumption that the most organic complexes are electronic, the results obtained rationalized considering the band theory of electronic conductivity[17]. The temperature dependence of mobility is a dominant factor in conduction that explains the increasing of conductivity at elevated temperatures. According to Wolden's rule, this is essentially a measure of the solvent "viscosity"[18] which suggests that temperature dependence of carrier concentration is the majority factor. The Wolden's rule does not obeyed in the case of run II (may be except for the
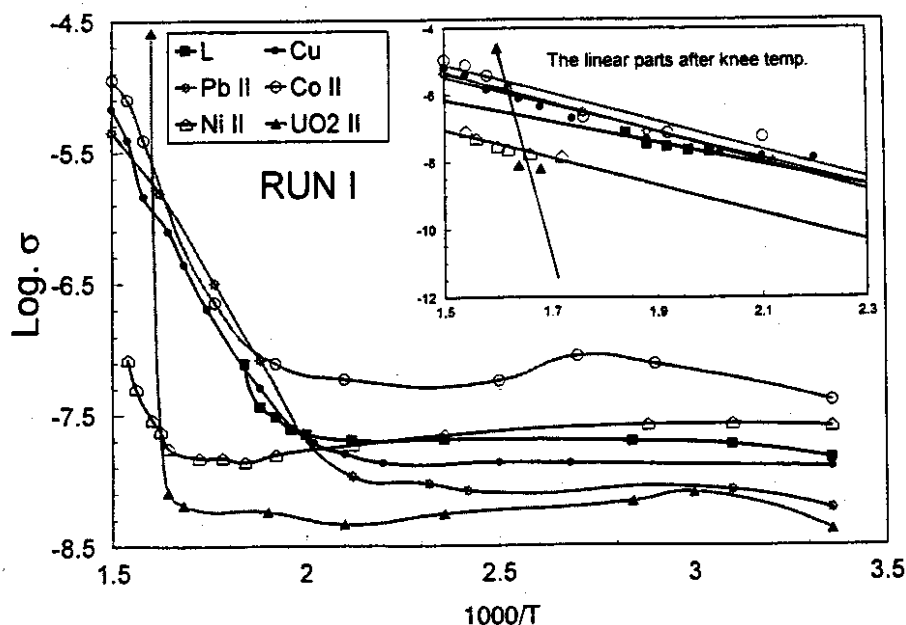

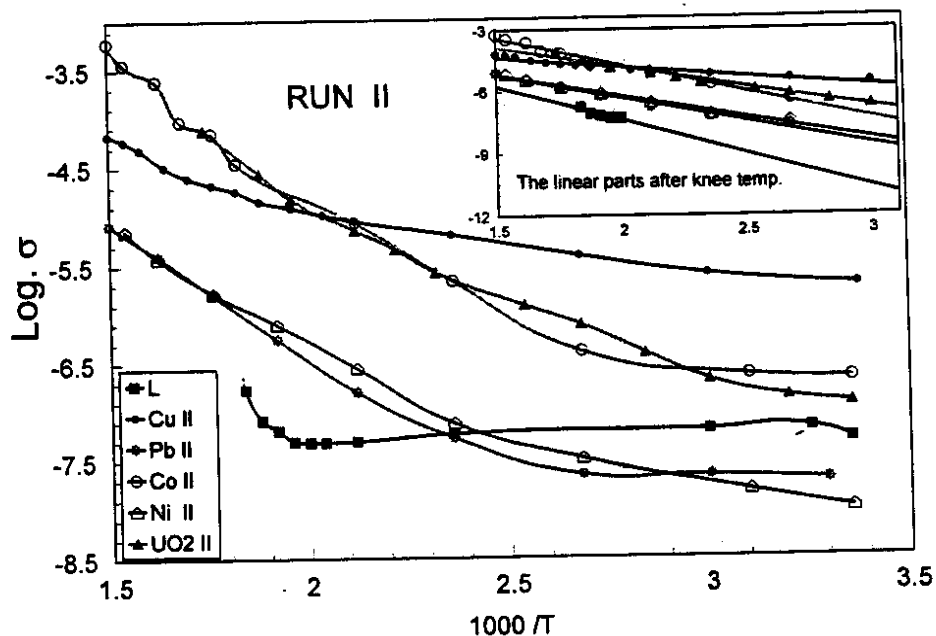Fig. 3a   Log. σ of the solid complexes before heat treatment vs 1000/T.

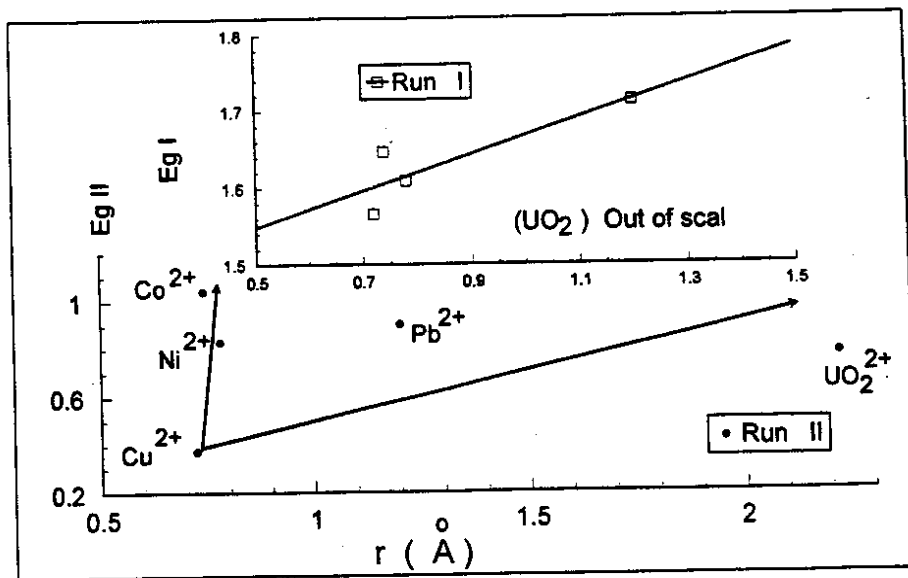Fig. 3b ; Log. σ of the solid complexes after heat treatment vs 1000/T.

Fig. 4   The relation between cationic radii and energy gaps before and after heat treatment.

ligand) where the knee temperatures are not present or very low.

The highest E_g obtained for unaryl complex (run I) indicates presence of two intermolecular hydrogen bonds between one of the perpendicular oxygen atoms of UO_2^{2+} and the neighbor hydrogen

of amino group (structure II g). At elevated temperatures the hydrogen bonds no longer exists and the lone pair electrons of oxygen atoms would sharing with the delocalized electrons raising the conductivity suddenly (more than 5.6×10^3 times) after long forbidden region Fig. 3a. The broken of two hydrogen bonds at elevated temperature is

Table 3: Electric properties of selected (DADCT) complexes before heat treatment.

(Run I)

comp	$r(\overset{O}{A})$	Knee T K	σ (Ωcm^{-1})	E_1 (ev)	m^* (g)	n (cm^{-3})	μ $cm^2V^{-1}s^{-1}$
L	—	488	2.233×10^{-8}	1.235	2.20×10^{-33}	2.571×10^{15}	5.428×10^{-5}
Cu II	0.72	454	1.325×10^{-8}	1.566	2.79×10^{-33}	6.591×10^{13}	5.203×10^{-3}
Co II	0.74	476	5.888×10^{-8}	1.647	2.93×10^{-33}	1.731×10^{13}	2.125×10^{-2}
Ni II	0.78	581	1.482×10^{-8}	1.609	2.86×10^{-33}	1.243×10^{15}	7.452×10^{-5}
Pb II	1.2	471	1.064×10^{-9}	1.713	3.05×10^{-33}	6.475×10^{13}	1.027×10^{-2}
U VI	0.83	595	5.530×10^{-8}	1.784		Out of scale	
UO$_2$ II	$\cong 2.23^*$						

* Summation of U^{6+} and $2O^{2-}$ diameters.

Table 4: Electric propertis of selected (DADCT) complexes after heat treatment.

(Run II)

| comp	$r(\overset{O}{A})$	Knee T °K	σ (Ωcm^{-1})	T °K	E_2 (ev)	m^* (g) $\times 10^{-33}$	n (cm^{-3})	μ ($cm^2 v^{-1}s^{-1}$)
L	—	500	1.259×10^{-7}	500	1.295	2.308	2.008×10^{15}	3.917×10^{-4}
Cu II	0.72	——	6.321×10^{-5}	500	0.371	66.070	1.419×10^{19}	1.056×10^{-5}
Co II	0.74	357	6.918×10^{-5}	500	1.039	1.850	2.849×10^{16}	1.157×10^{-2}
Ni II	0.78	400	1.318×10^{-6}	500	0.828	1.474	2.348×10^{17}	3.508×10^{-5}
Pb II	1.2	370	3.162×10^{-7}	500	0.898	1.599	1.176×10^{17}	1.679×10^{-5}
U VI	0.83	——	2.512×10^{-5}	500	0.771	1.373	4.089×10^{17}	3.839×10^{-4}
UO$_2$ II	$\cong 2.23^*$							

* Summation of U^{6+} and $2O^{2-}$ diameters.

similar to explosion of a bomb which throw out the unti-bonding electrons faraway (out of scale). The irregular behavior of uranyl complex did not appear in metal acetate complexes. This behavior indicates that the hydrogen bonds did not form between the carbonyl group of acetate and the amino group owing to the remoteness between them. This is the first time to use the EC measurements to investigate a part of structure.

Figure (4) shows the relation between the ionic radii of cations with (E_1 and E_2). In general the energy gaps increase with increasing ionic radii. This increasing could be attributed to the interaction between the electrons in d-orbital of the cations (or F-orbital of uranyl ion) with anti-bonding electrons which localized the π^* electrons charge in the ligand ($E^#$ increases). The cobalt (II) complex behaves similarly but in a different manner, may be due to the presence of two oxidation states of cobalt[19] which affects the interaction with π^* electrons.

The transition temperature (knee temp.) is proportional to the lattice defect[20] therefore we can assume about the increase in lattice defects as

shown. It has been seen that the heat treatment improved the lattice defect of all complexes.

increase of knee temperature
→
L-Cu^{2+}<L-Pb^{2+} < L- Co^{2+} < L<L-Ni^{2+} < L- UO$_2^{2+}$
→
increasing in lattice defect
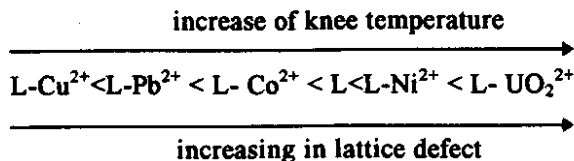
The electronic properties at elevated temperature before and after heat treatment are listed in tables 3 and 4. The concentration of the charge carriers (n) is calculated by using the following equation[7].

$$n = [2(2\pi m^* kT/h^2)^{3/2}] \; \exp [(-E^#/kT)] \qquad (2)$$

where m^* is the effective mass of charge carrier (assumed to be equal to the rest mass of electron), $E^#$ is the activation energy, and h is the Plank's constant. The mobility of the charge carrier (μ) can be calculated by using Johnson and Lark-Horowitz equation[21, 22].

$$\sigma = e \, n \, \mu \qquad (3)$$

where e is the charge of electron.

The significant effect on the activation energy is exerted by the complexation. The cations are not present as impurities (only if the cations conduct through similar mechanism of the ligand) and the complexes having an intrinsic semiconducting behavior. The mobility are low which is typical of organic semiconductors. The heat treatment increases the conductivities and decreases the energy gaps of all complexes by fixed the orientation of atoms and/or groups in new permanent phases having more stable structure. This behavior indicates that the heat treatment serves to increase the number of conducting charge n (increases the delocalized electrons of π - π^*, n - π^*, and d - π^* or f - π^*) and may be breakdown the weak bonds too (as hydrogen bonds), which increase the number of states available for conduction.

Experimental

Reagents:

The $Mn(CH_3COO)_2$. $4H_2O$, $Co(CH_3COO)_2$. $4H_2O$, $Ni(CH_3COO)_2.4H_2O$, $Cu(CH_3COO)_2$. H_2O, $Zn(CH_3COO)_2$. $2H_2O$, $Pb(CH_3COO)_2.3H_2O$, and $UO_2(CH_3COO)_2.2H_2O$ were chemically pure (Aldrich, Fluka) and have been used without further purification.

i)Synthesis:

The 2,4-diamino-3,5-dicyanothiophene (L, ligand = (DADCT)) was prepared as already described[6], the purity of the ligand have been checked by its infrared, ^1H and ^{13}C NMR and mass spectra at the Faculty of Pharmacy, Cairo University. The synthesis of 1,3-dicyano-2,4-diaminothiophene complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and UO_2^{2+} metal ions using the molar ratios of 1:1, 1:2 and 2:1 of metal ion to ligand respectively.

For the 2:1 metal ion to ligand ratio, all the complexes were prepared by simultaneous addition of 0.01 mole of the ligand and 0.02 mole of the divalent metal ion, both dissolved in absolute ethanol, with stirring for thirty minutes at room temperature, then reflux for about seven hours. The resulting solid was filtered out, washed with absolute ethanol then dried (all m.p. > 300 °C) .

ii) Spectral Measurements :

The mid-infrared spectra (4000 - 400 cm^{-1}) of the solid complexes (Fig. 1) were obtained with a KBr pellets using Perkin-Elmer infrared spectrophotometer model 1430 equipped with NaCl prism, the UV spectra (200-400 nm) have been recorded on Perkin-Elmer lambda 4B UV spectrophotometer (Fig. 2). For the X-ray measurements the substance was properly ground in an agate mortar then analyzed by means of a 1390 Philips type X-ray powder diffractometer using a Ni filter and Cu-K α-radiation. These measurements have been recorded at the Chemistry Department, Faculty of Science (girls), Ain Shams University, Cairo, Egypt. Additionally, Magnetic properties has been accomplished at Chemistry Department, Faculty of Science, Mansoura University (Johnson Metthey and Sherwood). Thermo-gravimetric analysis, Differential Thermal Analysis (Schimadzu DTA, TGA-50 H), and elemental analysis (nitrogen, sulfur and metal ions percentages) have been carried out at the Micro Analytical Center, Cairo University. All of the prepared complexes are 1 : 2 (LM$_2$) adducts of the ligand to the metal ion respectively (Table 1).

iii- Electrical Conductivity (EC) Measurements:

The EC measurements were recorded at the Chemistry Department, Faculty of Science (boys), Al-Azhar University, Cairo. The conductivity cell and the sample fabrication technique were the same as that reported before by Selim et al., [7]. The conductivity measurements were conducted with the polycrystalline sample disc pressed at 4 ton/cm^2, 1.0 cm diameter and thickness about 0.2 cm contained in a glass cell with Ni/Ni-Cr thermocouple in dry atmosphere. A silver paste used for electrical contact. The glass cell heated at desired temperature ± 2°C using an electrical furnace and the resistance recorded herein using a digital multimeter Escort EDM 2116 Chicago 11-60648. Two runs of conductivity measurement recorded for each sample, run I before applying heat treatment and run II on the same sample after heating above the transition temperature for two hours.

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