ELECTRICAL CONDUCTIVITY OF SALICYLALDEHYDE THIOSEMICARBAZONE AND ITS Pd(II), Cu(II) AND Ru(III) COMPLEXES

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Salicylaldehyde thiosemicarbazone complexes of Pd(II), Cu(II) and Ru(III) have been characterized by elemental analyses, molar conductance, infrared, NMR, electronic spectra and thermal analyses. The data show the formation of two different types of complexes with 1:1 and 1:2 metal:ligand stoichiometries. The *dc* electrical conductivity of the ligand and the complexes was measured at varying temperatures. The results obtained were explained and discussed in terms of proposed semicondutive behaviour of the complexes and a probable occurrence of phase transition. The activation energies were calculated for the ligand and the complexes.

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Introduction

The synthesis of transition metal complexes with thiosemicarbazone ligands has been receiving considerable attention due to the potentially useful chemotherapeutic properties of both ligands and complexes as antimalarial, antitumor and antibacterial activities.[1-3] The chemistry of thiosemicarbazone has received considerable attention because of their variable bonding modes, promising biological implications, structural diversity, and ion–sensing ability.[4,5]

Thiosemicarbazones usually behave as chelating ligands against transition and non-transition metal ions binding through sulphur and nitrogen atoms, although in few cases they act as unidentate ligand with sulphur as the binding atom.[6] Platinum group metal complexes show a broad spectrum of pharmacological activity.[7] It was found that their dibasic tridentate thiosemicarbazones with ONS donor sites are of immense importance as they possess a wide spectrum of medicinal properties and can also give dimetallic or polymeric species with unusual structural and magnetic properties.[8]

In this paper, we report the synthesis and characterization of some salicylaldehyde thiosemicarbazone complexes of Pd, Cu and Ru. The d.c. electrical conductivity and thermal analyses have been correlated and their ΔE_g for conduction have been discussed.

Experimental

The ligand was prepared by mixing equimolecular amounts of thiosemicarbazide and salicylaldehyde in absolute methanol and refluxing on a water bath for two hours, the condensation products was filtered off, crystallized form methanol and dried under vacuum. The metal complexes were prepared by mixing 1:1 or 1:2 molar ratios of Cu(II), Pd(II) and Ru(III) salts and the ligand, respectively, in absolute methanol. The mixtures were refluxed on a water bath for a time depending on the nature of metal cation used. The formed complexes were filtered off, washed several times with pure dry methanol, and dried under vacuum. Elemental analyses (C, H, Cl) were performed at the micro-analytical unit of the University of Cairo. Pd and Cu were determined by established methods.[9] DTA. and TGA were carried out on a Shimadzu DT-30 and DT-50 thermal analyzers. Molar conductance was measured in DMF (DMSO for Pd complexes) using a Bibby conductometer type MC-1. The electronic and IR spectra were recorded on Perkin Elmer Lambda 4B UV-VIS. and infrared spectrophotometers, respectively. Magnetic susceptibilities were measured by the modified Gouy method using $Hg[Co(CNS)_4]$ as a calibrating agent and a Johnson Mathey magnetic susceptibility balance. Diamagnetic corrections were made using Pascal's constants.[10] The magnetic moments were calculated from the equation: $\mu_{eff}=2.84(\chi_m^{corr}T)^{1/2}$ the electrical conductivity was measured as given earlier using Keithly 616 electrometer.

Biological activity. The preliminary screening test was performed by the disk diffusion methods.[11,12] Whatmann No.1 filter paper discs (6 mm diameter) were sterilized by autoclaving for one hour at 120 ˚C. The sterile discs were placed on the surface of the cold solid medium in Petri-dishes inoculated with the microorganism and then incubated at 28 ºC. The inhibition of the microbial growth was evaluated after 24 hours.

Results and discussion

The elemental analyses, physical and analytical data of the investigated complexes were summarized in Table 1. All the complexes are quite stable at room temperature and non-hygroscopic in nature. The complexes are freely soluble in DMF, DMSO, and pyridine. The values indicates that the molar conductance complexes I and IV are non-electrolytes, whereas complexes II and III are univalent electrolytes. The insolubility of the complexes in common organic solvents and non-melting nature indicate that they are polymeric or ionic.[13]

Electronic spectra and magnetic moment

Pd(II) complexes are diamagnetic suggesting square planar geometry for these complexes. Electronic spectral data and assignment (Table 1) are also indicative of square planar geometry. Also, Ru(III) complex magnetic moment is 0.96 B.M. Which is less than the low spin d^5 configuration indicating magnetic exchange interaction between Ru(III) ions, this could be explained by a dimer formation through chloride bridges.[14]

The ligand exhibits a solid state electronic spectral band at 389 nm which is assigned to n-π* transition associated with the thiosemicarbazone moiety $C=N^1$. This band is blue shifted to ca. 323 nm and 370 nm in palladium complexes respectively.[15] Also, the complexes show a non ligand band at ca. 411 nm due to charge transfer.[15]

In the UV-VIS spectrum of the ligand solution, the absence of π-π* of C=S group at 238 nm[16] indicates the thiol form[17] and the presence of two bands at 343 and 332 nm assigned to n-π* transition of azomethine chromophore confirming that the ligand contains the azine group and the ligand in the solution is present in its thiol form (Figure 1).

In the complexes (I and III), the band assigned to the n-π* at 345 nm greatly decreases in the intensity indicating that $C=N^1$ group is coordinated to the metal ion. The absence of the band corresponding to the $C=N^2$ group is a good evidence that the ligand in these complexes is present in the thione form, this is supported by the appearance of C=S band at 224 nm. The intraligand bands for complexes II and IV are present at ca. 343 and 333 nm corresponding to n-π* transition of $C=N^2$ and $C=N^1$ groups with large molar absorptiveness due to the increased conjugation of the ligand and the absence of π-π* of C=S indicates that complex II contains the ligand in the thiol form. The complexes show also non-ligand bands due to charge transfer at 370-407 nm.[18] The spectrum of the copper(II) complex displays the d-d transition band at 622 nm, suggesting square planar geometry.[19] This also supported by the lower value of the effective magnetic moment (μ=1.13 B.M) due to metal-metal interaction[20] in the dimeric structure.

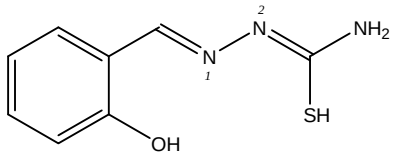


Figure 1. Structure of the ligand

1H NMR spectra

The ^{1}H NMR spectrum of the ligand in DMSO shows the phenolic OH proton at 11.4 ppm and the NH proton at 9.9 ppm, these two peaks disappeared in the presence of D_2O. The spectra of complexes I and II in DMSO are similar to that of the ligand except that in the spectrum of complex I the signal due to OH proton disappeared while that of the NH proton appeared. This indicates that the palladium is bonded to the phenolic OH and azomethine nitrogen; on the other hand the spectrum of complex II shows the presence of the phenolic OH at the same position while the NH protons disappeared.

Table 1. Analytical and electronic spectral data of salicylaldehyde thiosemicarbazone and its Cu, Pd, and Ru complexes

Compound	Colour	MP or (d.p.) ºC	Λ_m	Elect-rolyte nature	Found (calcd.) %[b]				Intraligand and Charge Transfer (molar absorptivities*10^{-4})				μ_{eff} B.M.
					C	H	M	Cl	C.T.	n→π* $C=N^1$	π→π* $C=N^2$	n→π* C=S	
Ligand [H_2L]	Bright yellow	219-221	3	[a]	49.3 (49.5)	4.9 (4.8)	- -	- -		343 (3.00)	332 (2.8)		-
Complex I [Pd(HL)Cl]	Brown	>300	60	[a]	28.7 (28.6)	2.7 (2.4)	32.6 (31.7)		387 (062)	345 (0.56)		223	Dia
Complex II [Pd(H_2L_2)Cl_2]	Orange	275	151	1:1	33.3 (33.2)	3.2 (3.2)	18.3 (18.8)	13.4 (12.5)	383 (1.2)	344 (2.6)	333 (2.2)	-	Dia
Complex III [Cu(HL)Cl]	Dirty green	280	121	1:1	32.4 (32.8)	3.5 (2.7)	20.9 (21.7)	12.8 (12.1)	622 (0.07) 407 (0.26) 371 (0.4)	346 (0.32)		225	1.13
Complex IV [RuLCl·H_2O]	Black	>300	41	[a]	27.6 (27.6)	3.2 (2.6)	29.5 (29.1)	9.8 (10.2)	407 (0.33) 370 (0.28)	347 (0.37)	338 (0.41)	-	0.96

[a] Non-conducting solution, [b] % H_2O 5.7 (5.2).

IR spectra

The ligand

The IR spectrum of the ligand (Table 2) exhibits phenolic group frequencies ν(OH), oop(OH) and ν(C-O) at 3440, 950 and 1273 cm^{-1} respectively and exhibits also a strong band at 1612 cm^{-1} assigned to (C=N).[21] The appearance of a band at 1056 cm^{-1} is assigned to (C=S)[22] which is a good evidence that, in the solid state the ligand is a mixture of free syn and hydrogen bonded anti forms (Figure 2).

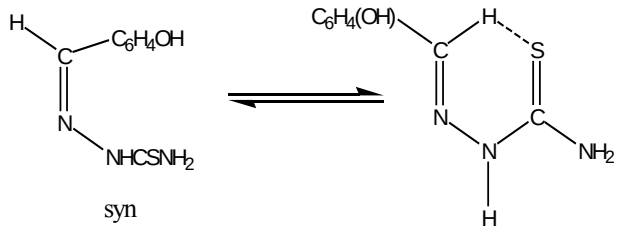


Figure 2. Ligand structure in the solid state

The complexes

Comparison of the IR spectra of I and III complexes with that of the free ligand reveals the absence of bands corresponding to phenolic (OH) and (C=N) groups. The band assigned to (C=S) is shifted to lower frequencies compared to that of the ligand; while the (C-O) band is shifted to higher frequency indicating that the phenolic OH is deprotonated and that Pd and Cu are bonded through the azomethine nitrogen,[17,20] C=S[22] and phenolic oxygen.[23]

In the spectrum of complex II, bands corresponding to free phenolic OH, which is proved by the violet color appearing during the addition of aqueous $FeCl_3$ solution to its alcoholic solution. On the other hand, the disappearance of ν(C=S) and δ(N-H) and appearing of three news bands at 2587, 601 and 1595 cm^{-1} assigned to V(S-H),[24] ν(C-S)[25,26] and ν(C=N-N=C)[27], respectively, indicating that palladium is coordinated through the azomethine nitrogen and thiol sulphur whereas the phenolic OH is still free. In the Ru complex the disappearance of ν(OH), ν(NH), (C=S) accompanied by the appearance of bands at 1595, 619 cm^{-1} due to ν(C=N-N=C)[27] and ν(C-S)[25,26] indicates that Ru is bonded through O, N and S atoms. The presence of water in Ru complex is indicated by the presence of a broad band around 3400 cm^{-1} which could be assigned to δ(OH) stretching.[28] The presence of non-ligand bands at ca (503-510) (522-543), (414-430) cm^{-1} proves coordination through O,[23] N,[21] S.[25,26]

Based on the previously discussed elemental analyses, conductance, magnetic moment, electronic and IR spectra, the structure of the investigated complexes can be represented as in Figure 3.

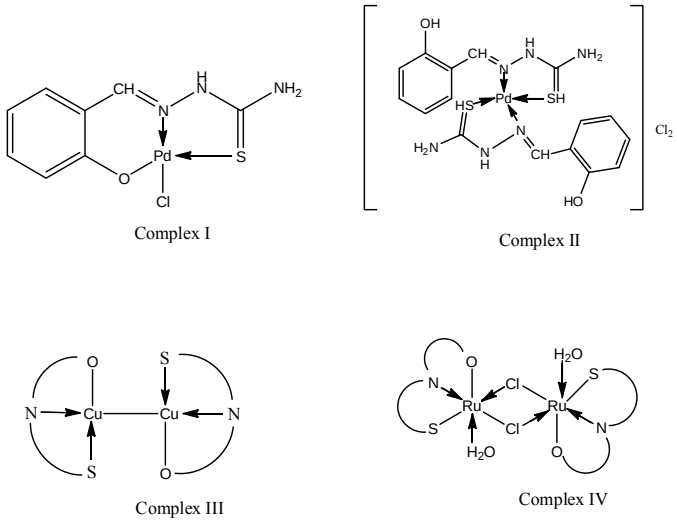


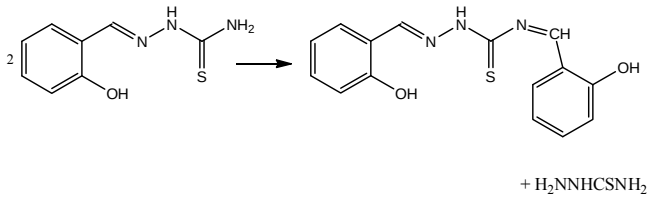
Figure 3. Proposed structure for the investigated complexes

Thermal analyses

Salicylaldehyde thiosemicarbazone is thermally stable up to 225˚C. The medium endothermic peak at 220 ºC (without weight loss) is due to its melting. The exothermic peak at 237 ºC with 25.5% weight loss may be due to the loss of one molecule of thiosemicarbazide from two molecules of the ligand according to scheme 1.

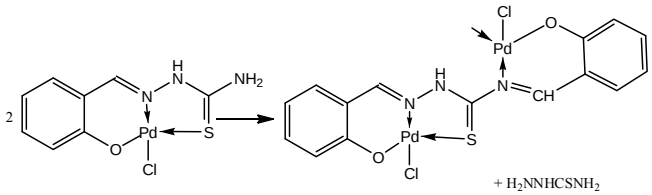
Table 2. IR spectral data of salicyaldehyde thiosemicarbazone and its Cu, Pd and Ru complexes

Compound	ν(OH) δ(OH)	ν (NH)	ν (S-H) ν (C-S)	ν (C=N)	ν (C=S)	ν (M-O)	ν (M-N)	ν (M-S)
Ligand [H_2L]	3340(S) (950)m	3317(s) 3170(d)	- -	1612	1056(m)	-	-	-
Complex I [Pd(HL)Cl]	- -	3302(w) 3133(w)	- -	1599(m)	1036(m)	503(m)	522(w)	414(m)
Complex II [$Pd(H_2L_2)Cl_2$]	3415(s) (946) (m)	3327 3255	2587 (601)	1595(m)	-	-	543	423
Complex III [Cu(HL)]Cl	- -	3378 3178	- -	1604	1028	517	532	433
Complex IV [$RuLCl{\cdot}H_2O$]	broad	3262 3139	- (619)	1604	-	510	530	440



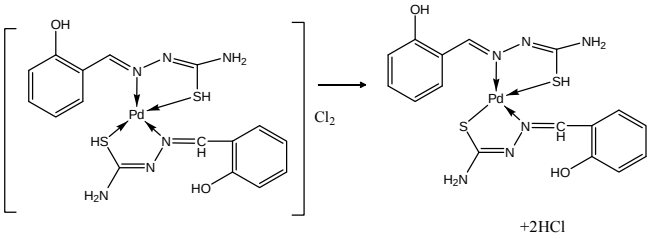
Scheme 1. Thermal decomposition of the Ligand

Complex I decomposes at 370-390 ºC after rearrangement at 300 ºC and before its melting at 320 ºC (Table 3). The decomposition is similar to that of the ligand that occurs by losing one thiosemicarbazide molecules from two molecule of complex according to Scheme 2.



Scheme 2. Thermal decomposition of complex I.

Complex II: after rearrangement at 200 ºC, it melts at 260-285 ºC losing two molecules of HCl resulting in the formation of the 1:2 inert complexes according to Scheme 3.



Scheme 3. Thermal decomposition of complex II.

D.C. electrical conductivity

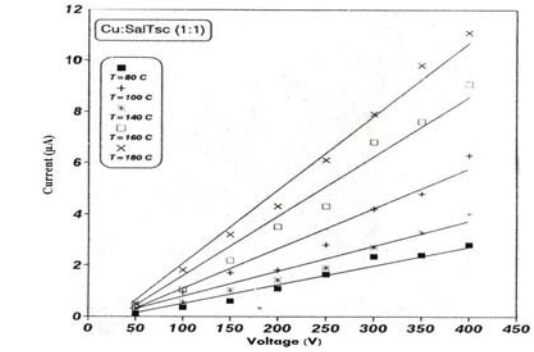
The I-V (current intensity-voltage) characteristic curves of the ligand (Figure 4) and its complexes were measured in the temperature range of 20-180 ºC and the voltage range of 0-400 volts. From this Figure, it is clear that, the I-V curves obey the well known Ohm's law in certain temperature and voltage ranges. The amount of respond current, which reflects the sample conductivity, was found to vary from a sample to another, and the current-voltage dependence seems to be approximately linear in certain ranges. In ranges, which almost follow the linear I-V range, we found that by increasing the applied voltage by very small amount, the current is sharply increased causing the so called switching voltage and it was a function of temperature. To elucidate this observation we built new sample holder with pin electrode to measure accurately the I-V curves in the switching range.

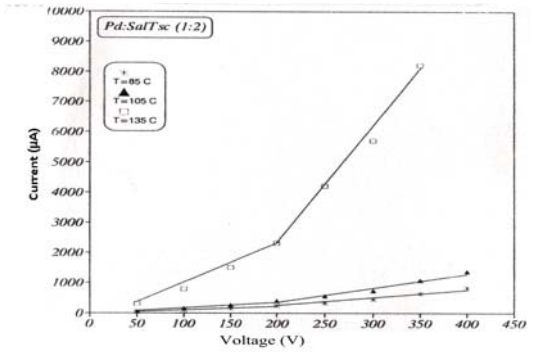
Figure 5 shows the temperature dependence of the d.c. electrical conductivity of the ligand and complexes. From this figure, it is clear that, the samples exhibit a semiconducting behaviour in a certain temperature range from which the activation energies ΔE were calculated using the well known Arrhenius equation.

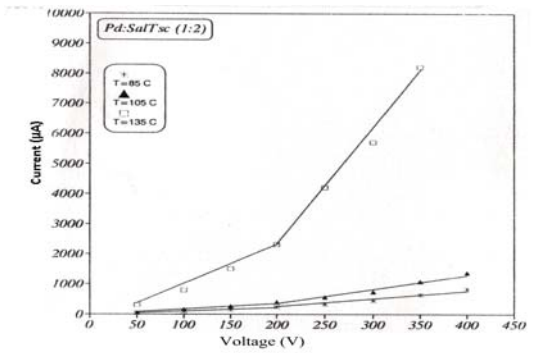
From these measurements: we observe that the conduction mechanism of the ligand and complex I is electronic where the conductivities at 110 ºC is of the order of -10.1 and -10.6 Ω^{-1} cm^{-1} respectively and the activation energies are about 0.55 and 0.53 eV, respectively. For complexes II, III and IV, where the conductivities were very high, the activation energies for conduction were very low. In these complexes values of log σ at t = 110 ºC are -7.8, -2.27, and -1.35 Ω^{-1} cm^{-1}, respectively and the activation energies are 0.29, 0.12, and 0.43 eV, respectively. These complexes have two halogens in their structures which enhance the conductivity and may act as an agent charge carrier transport.

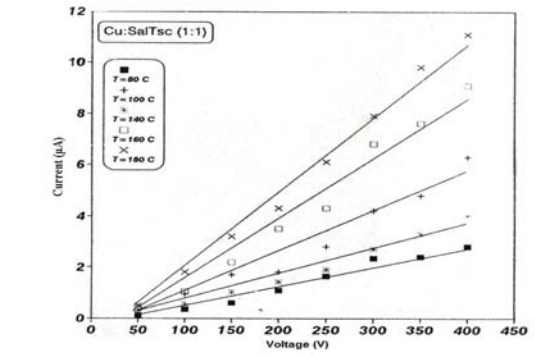
Table 3. Thermal analyses data of the ligand and its Pd complexes

Formula	M. wt	Temp. ºC	%wt. loss Calc. (Found)	DTA peaks	Temp. ºC	Assignment
Ligand [H_2L]	195	220	-	endo(m)	220	Due to melting
$C_8H_9N_3O_5$		220-256	23.3 (25.5)	exo (m)	237	Loss of thisemicarbazide according to scheme 1
		270-500	-	-	-	Stable
[Pd(HL)Cl]	336	80	- (-)	-	80	Due to rearrangement
		320	13.5 (16.0)	endo	320	Due to melting
		370-390		exo(br)	390	Loss of thiosemicarbazide according to scheme 2
		390-500		-	-	Stable
[Pd(H_2L_2)Cl_2]	567.5	100	-	endo	100	Due to rearrangement
		260	-	endo	260	Due to rearrangement
		260-285	12.9 (13.0)	exo	270	Loss of 2HCl molecules according to Scheme 3
		285-395	-	-	-	Stable
		395-500	-	-	-	Further decomposition









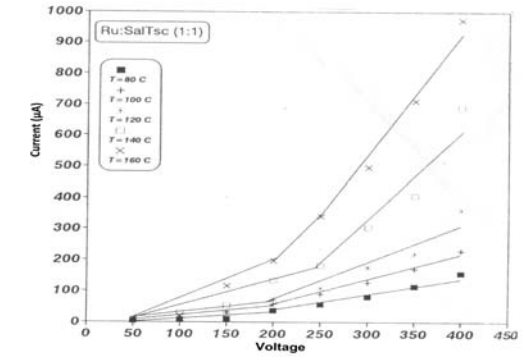
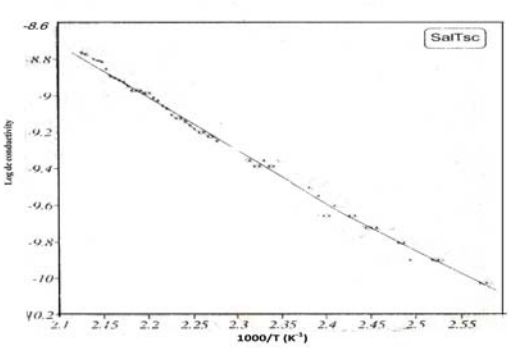
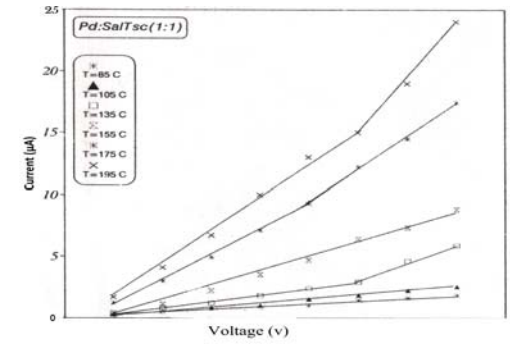
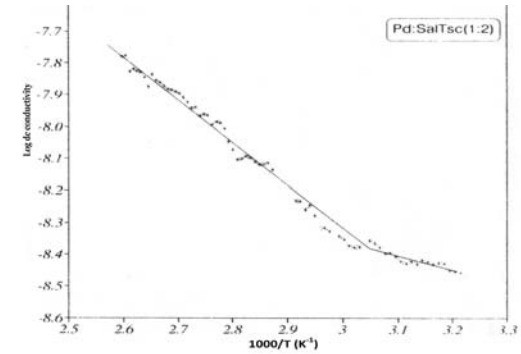
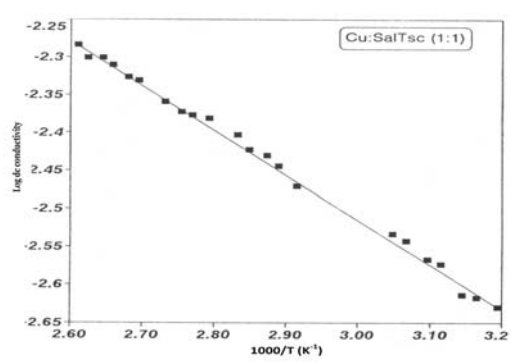


Figure 4. *I-V* characteristic lines of salicyaldehyde thiosemicarbazone (SalTSC) and its complexes









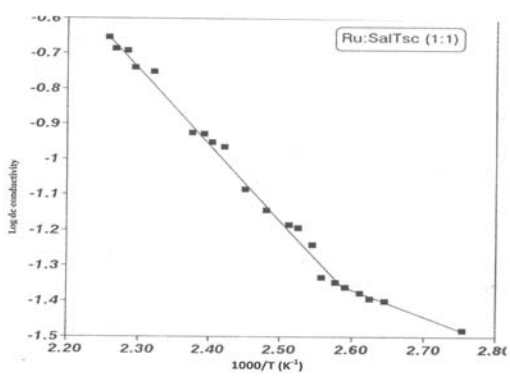


Figure 5. log *dc* conductivity vs. 1000/*T* of salicyaldehyde thiosemicarbazone (SalTSC) and its complexes

Biological activity

The biological activity of the ligand and its complexes are summarized in Table 4. From this table, it is clear that the ligand has antimicrobial activity nearly as the control (DMSO), which means that it has activity neither to gram positive nor negative bacteria. Also, the Ru complex is inactive against both of them. On the other hand the copper complex has a very high antimicrobial against gram-positive and gram-negative bacteria, whereas, the palladium complex shows less activity than the copper complex against both. This is agreeing with what reported by Scovill et al.[29] that complexed thiosemicarbazone, especially copper(II) and iron(III) are more active than uncomplexed ones. Also, it is clear from Table 4 that neither the ligand nor its complexes have activity against fungi.

Table 4. The preliminary screening of antimicrobial activity of salicylaldehyde thiosemicarbazone and its complexes

Compound	Gram +ve	Gram -ve	Fungi
	Bacillus subtillus	Escherichia Coli	Candida Libolica
Ligand	6.0	7.0	6.0
Complex I	9.3	8.1	6.0
Complex II	11.1	9.0	6.0
Complex III	16.0	16.0	6.0
Complex IV	6.0	6.0	6.0
Complex V	6.0	6.0	6.0
DMSO	6.0	6.0	6.0

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