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ELECTRICAL CONDUCTIVITY PROPERTIES OF SOME O-SUBSTITUTED ARYLAZO - BARBITURATE COMPLEXES AT DIFFERENT TEMPERATURES

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Electrical conductivity properties of some *o*-substituted arylazo-barbiturate complexes at different temperatures are studied. The σ_o, ΔE and E_g values are determined. The copper complexes derived from $-H$, $-CH_3$ and $-OCH_3$ substituted organic compounds are with semiconducting properties at low temperatures and insulator at high temperatures. All the carboxy and the cobalt and the the nitro complexes, and nickel-methyl complexes are of semiconducting behaviour. The data are explained in the light of extrensic and lattice vibrations and the width of the forbidden energy gap properties.

The measurements of electrical conductivity are useful to indicate the overall order of the conductivity of a material. However, as detailed assessment of the relationship between the electrical conduction parameters and "chemical molecular" is very dangerous. In our laboratory [1-21], the synthesis and characterization of azo compounds and their metal complexes have been investigated. As a continuation of the chemical properties of the structural chemistry of these systems at different temperatures, it is desirable to throw light on the mechanism of electrical conductivity of 5-(*o*-substituted phenyl-azo)-barbituric acid complexes at different temperatures and related to their physicochemical properties. The σ_o, ΔE and E_g values are evaluated. The data are related to the chemistry of the transition metal

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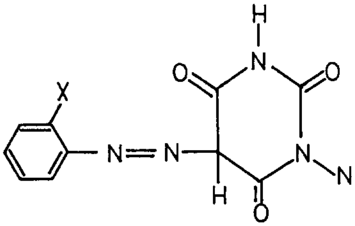
ion and the electronic character of the substituents. The *I-V* characteristic of these complexes to obey the ohmic nature is investigated.

Experimental

The organic compounds and their complexes were prepared as reported [22]. The general structural formula for these compounds are given as follows;



X = $-H$, $-NO_2$, $-CH_3$, OCH_3 and $-COOH$

Where H_2L stands for all the organic compounds except the carboxy (the latter is represented by the symbol, H_3L). The complexes are prepared by mixing the required weights of both the transition metal chloride salt with the corresponding organic compound, both dissolved in ethanol. The complexes were separated and filtered and then dried in vacuum desiccator over P_4O_{10}. The analytical data of complexes are given. For the $-CH_3$ organic compound, the complexes are $Co_2L \cdot 2H_2O$; $NiL \cdot 2H_2O$ and $Cu(HL)_2 \cdot 2H_2O$. However, the prepared carboxylic complexes are $Co(HL) \cdot 2H_2O$, $Ni(HL)_2 \cdot 2H_2O$ and $Cu(HL) \cdot 2H_2O$. On the other hand, the synthesized nitro complexes are $Co(HL)_2 \cdot 3H_2O$, $Ni(HL)_2 \cdot 3H_2O$ and $CuL \cdot 3H_2O$. But the -H and $-OCH_3$ ligands gave only the corresponding copper complexes of the formula $Cu(HL)_2 \cdot 2H_2O$ and $CuL \cdot 2H_2O$, respectively.

The electrical conductivities of the prepared complexes were measured in the temperature range 285-666.7 K on a Keithely 175 autoranging multimeter with an applied volt 200 V and a rate of heating 1 deg/min. The samples were prepared in the form of tablets of thickness 0.1-0.3 cm at a pressure of about 5 ton/cm^2. The samples were held between two copper electrodes with silver paste and then inserted with the holder vertically into a cylindrical electric furnace. The conductivity of the sample was obtained during heating using the general equation: $\sigma = \frac{I}{V_c} \cdot \frac{d}{a}$ where (I) is the current in ampere and (Vc) is the potential drop across the sample of cross-sectional area (a) and thickness (d).

Results and discussion

The variation in the logarithmic electrical conductivity values as a function of the reciprocal absolute temperature for these complexes are represented in Figs (1-3). The dependence of the conductivity of the semiconducting materials on temperature is expressed by the equation:

$$\sigma = \sigma^{*} e^{-\Delta E/KT}$$

where ΔE is the activation energy for the conduction. σ^{*} is a constant for the conductivity independent of temperature and K is the Boltzmann constant. The values of electrical conductivity (σ_o), activation energy (ΔE) and the energy gap (E_g) of these complexes are collected in Table 1.

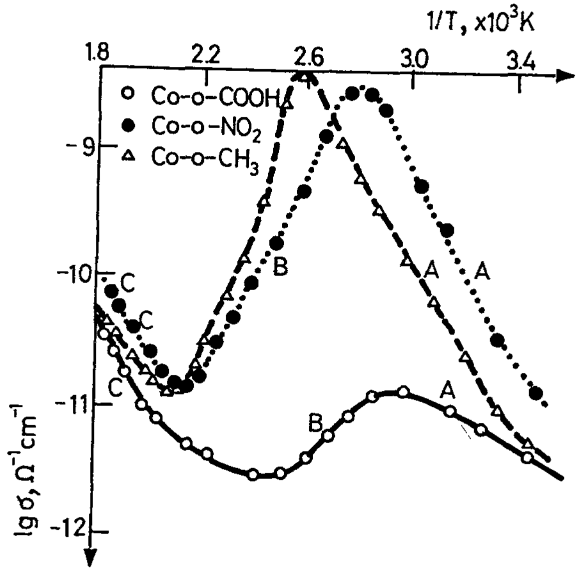


Fig. 1 logσ *vs.* 1/T relationskip for the cobalt complexes

Table 1 Conductivity data

Compound	$\log\sigma_o$	ΔE_A	ΔE_B	ΔE_C	$2\Delta E_A$	$2\Delta E_B$	$2\Delta E_C$
$-CH_3$							
$(Co)_2L\cdot 2H_2O$	–9.8	1.33	1.87	0.93	2.66	–3.74	1.86
$NiL\cdot 2H_2O$	–11.1	0.75, 1.83	–2.27	1.22	1.5, 3.66	–4.54	2.44
$Cu(HL)_2\cdot 2H_2O$	–6.2	–	–	5.48	–	–	10.96
$-COOH$							
$CoHL\cdot 2H_2O$	–9.42	0.44	–0.69	0.48, 1.6	0.88	–1.38	0.96, 3.2
$Ni(HL)_2\cdot 2H_2O$	–12.78		–0.14	0.13, 0.84		–0.28	0.26, 1.68
$CuHL\cdot 2H_2O$	–11.82	0.55	–1.0	–	1.10	–2.0	–
$-NO_2$							
$Co(HL)_2\cdot 3H_2O$	–9.38	1.42	–1.70	1.13	2.84	–3.4	2.26
$Ni(HL)_2\cdot 3H_2O$	–10.90	0.30	–0.15	0.61	0.60	–3.00	1.22
$CuL\cdot 3H_2O$	–11.60	0.23	–0.24	–	0.46	–0.48	–
$-OCH_3$							
$CuL\cdot 2H_2O$	–10.9	0.44	–	–	0.88		
$-H$							
$Cu(HL)_2\cdot 2H_2O$	–10.28	0.93	–1.85	0.04, 0.9	1.86	–3.70	0.08, 1.8

ΔE = Activation energy, $2\Delta E$ = Energy gap

These results allowed the following observations:

a) The curves of the Cu-*o*-CH_3 complex reveals a negative temperature coefficient of resistance $\left(\frac{dR}{dT}\right)$ with a conventional semiconducting behaviour, Cu-*o*-OCH_3 complex shows a constant conductivity value in the temperature range (12-47.5°), Fig. (3), to argue that this complex possess insulator properties under these conductions.

b) The temperature dependence of the conductivity curves of the cobalt and nickel complexes of the *o*-methyl and those of carboxy and nitro complexes and Cu-H complex exhibit three regions: *A*, *B* and *C* Figs 1-3. In some cases the regions *A* and *C*, with a positive temperature coefficient of electrical conductivity. The region *B* has a negative value. Thus, the electrical activation energies of these complexes reveal positive values in the regions *A* and *C* but negative in *B*. The region *A* exhibits an increase of conductivity as the temperature is increased with a relatively low activation energy due to the activation from the donor level to the conduction band i.e. and extrensic behaviour. The region *B*, is characterized by the decrease of conductivity as the temperature is increased. This results of scattering of carriers by photons, due to lattice vibrations within the temperature range covering this part. The slope of line *B*, Table 1, and its temperature range vary widely depending on the nature and the structure of the complex. The region *C* has a positive temperature coefficient with an activation energy higher than that of region *A* (with exception of the cobalt-methyl and nitro-complexes). Thus, this part is the interensic region of conductivity, when the conduction is from the valence band to the conduction band. However, the curves of nickel, copper carboxy and copper nitro complexes do not show all the three lines. This is more likely due to the width of the forbidden gap. The high activation energy values of cobalt complexes of methyl and nitro ligands is probably connected to the electronic transition between the valency bands or the localised levels to the conduction band. However, the low activation energies are related to the electron hopping which is thermally activated process [23]. This may be the result of a relatively weak electronic coupling between the donor and the acceptor molecules [24]. The phenomenon of discontinuation observed in the electrical conductivity-temperature relationship showed two or three segments with variable activation energies, probably due to the presence of different crystallographic or phase transitions [25]. All the complexes are with low conductivities of semiconducting properties (Table 1). Hence, the electrons in the available orbitals of the complexes are not of high mobility. The ΔE or σ_o values of the complexes gave that all the copper complexes are strongly affected by the electronic character of the substituent, where as the electronegativity increases, the ΔE value is decreased. For part *A*, the ΔE value is arranged in the following order: -H > -COOH ≥ $-OCH_3$ > $-NO_2$. However, for the $-CH_3$, -COOH and $-NO_2$ complexes, the ΔE value for region (*A*) is decreased as the atomic number increases. This indicates that the holes in the system has little effect on the mobility of charges, except for the Cu-*o*-COOH complex [26]. This could be explained on the bases that the metal orbitals interact with that of the organic compounds to give new molecular orbitals, which are delocalized over the whole molecular complex. The relevant ligand orbitals transform as B_{1u} and B_{2g} which may interact with $4p_z$ and $3d_z2$ orbitals, respectively. The B_{1u} type MO's are sufficiently stabilized on the interaction with the $4p_z$ orbital to become occupied [27]. However, the first step for conduction is the excitation of Π electron from the uppermost filled Π-orbital to the lowest empty-MO [28, 29]. The electron is then assumed to tunnel to the equivalent empty level of the neighbouring molecule in the direction of the anode, whereas the positive hole is moving in the opposite direction towards the cathode. If initial excitation is involved in the complexes, it is no longer necessary that the electron in the uppermost Π-level comes from the

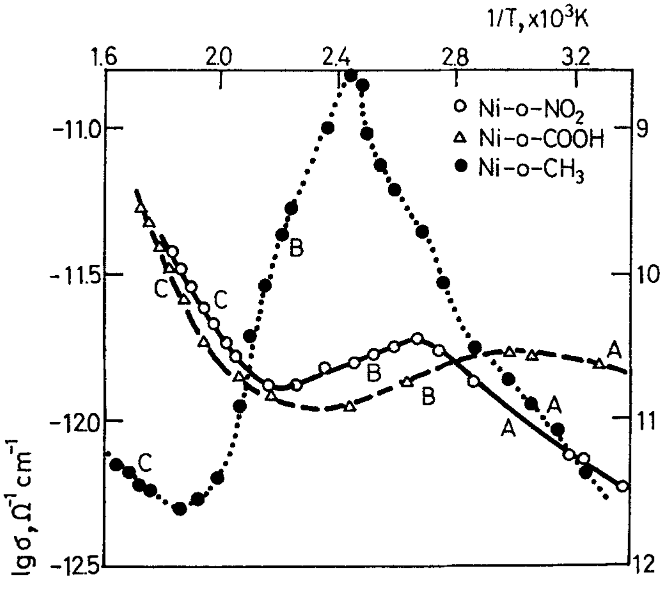


Fig. 2 log*σ* *vs*. 1/*T* relationship for the nickel complexes

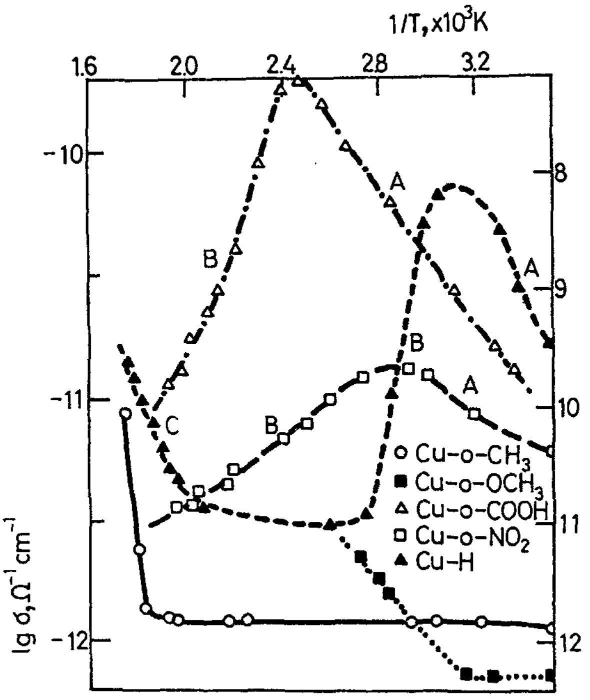


Fig. 3 logσ *vs.* $1/T$ relationship for the copper complexes

highest occupied MO as it arises from a positive orbital centre. If the electron is assumed to arise from the highest MO, it must be placed in a state of different multiplicities in order to become sufficiently long-lived. The first excited singlet and the first triplet state will almost certainly be too far above the ground state to allow thermal population. This assumes that the population of electrons in the lowest unoccupied Π-MO depends on the absolute anergy of the lowest empty orbital in the complexes [30]. In the most complexes, during thermal agitation an additional increase in the electrical conductivity occurs, probably indicating a discontinuity of the chemical bond existing in the compounds. However, the following extra comment are observed:

1) The $\log\sigma - \frac{1}{I}$ relation for the Ni-CH3 complex gives two segments, the first lies within the temperature range 12.7-86.7°, followed by the second one up to 135°. The first is due to the dehydration of the complex (i.e. loss of water in outer sphere) and the second is due to the lattice defect of

dehydrating the complex. The latter region is characterized with a strong increase in the conductivity values with a high activation energy.
2) For the Co-COOH and Cu-H complexes, a separting region between the two segments is appeared at 0.5 eV. This probably due to presence of a transition state between lattice geometry to the internsic form.

Although the copper atom contains one more electron than the nickel atom, this electron will occupy the $d_{x2\text{-}y2}$ orbital and will be likely takes part in intermetallic interactions. It seems in case of the –*o*–NO_2 complexes that as the molecular weight increases, the conductivity increases.

However, on correlating the mobility values to those of the conductivity, best fit straight lines pass with the origin are obtained with a slope equals to $6.25\cdot10^{-3} \pm 0.02\cdot10^{-3}$. This points that these complexes can be used as applied materials in the field of conductivity.

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Zusammenfassung — Bei verschiedenen Temperaturen wurden die elektrischen Leitfähigkeitseigenschaften einiger *o*-substituierter Arylazobarbiturat-Komplexe untersucht und Werte für σ_o, ΔE und E_g ermittelt. Die durch H–, CH_3– und OCH_3–Substitution der organischen Verbindungen erhaltenen Kupferkomplexe zeigen bei niedrigen Temperaturen Halbleiter- und bei hohen Temperaturen Isolatoreigenschaften. Alle Carboxy- und Nitrokomplexe sowie die Kobalt- und die Nickel-Methyl-Komplexe zeigen Halbleiterverhalten. Die Ergebnisse werden angesichts von Störstellen- und Gitterschwingungen und der Breite der verbotenen Energiezone erklärt.