

Electrical properties of some 3-azomethine-2-methylbenzopyrrole derivatives and their transition metal complexes

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Abstract

The electrical conductivity properties of the Schiff bases derived from reaction of 2-methylbenzopyrrole-3-carboxaldehyde with some aniline derivatives, and their metal complexes, were studied. It has been concluded that the metal complexes have slight semiconducting behaviour. Their conductivity and activation energy were found to depend on molecular structure as well as the ionic radii of the metal ions. The mechanism of conduction was also investigated. In addition, the current–voltage dependence of the metal-free ligands and of some metal complexes was studied. This indicates that the metal-free ligands have ohmic conduction which is temperature-independent. However, the metal complexes were found to vary from ohmic and/or space charge limiting current conduction over the different ranges of applied voltage.

INTRODUCTION

Recently extensive research concerning the development of new organometallic polymers with semiconducting and conducting properties has been reported [1,2]. These materials open up the possibility of designing and synthesising unique substances of both fundamental and technological interest. In these compounds the metal d orbitals may overlap with the π orbitals of the organic ligands and thereby extend electron delocalisation along a molecule. The present work is an extension of previous work on the synthesis and physicochemical properties of Fe(III), Co(II), Cu(II), Ni(II) and Mn(II) complexes with some Schiff bases [3]. It is aimed at studying in detail the electrical conductivity, the mechanism of conduction and the current–voltage (I – V) characteristics of these complexes.

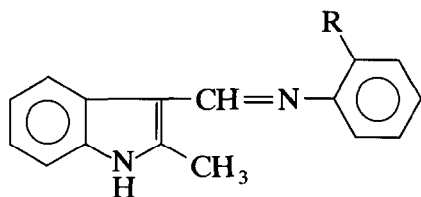
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EXPERIMENTAL

The Schiff base ligands under investigation **I**, **II** and **III** were synthesised according to the usual procedures. The general structural formulae of these ligands are given in Scheme 1.

A series of metal chlorides, in addition to copper acetate complexes with ligands **I–III**, were synthesised and characterised as described elsewhere, [3]. The formulae of these complexes are presented in Table 1.

The electrical resistivities were measured for samples of both the ligands and their metal complexes in the form of discs (diameter 13 mm and thickness 1–2 mm). These were prepared by compressing the powders at a



Scheme 1. **I**, R = OH; **II**, R = COOH; **III**, R = $\begin{array}{c} \text{O} \\ \parallel \\ \text{As}(\text{OH})_2 \end{array}$.

TABLE 1

The electrical conductivity at 30°C ($\log \sigma$), activation energies ΔE_1 , ΔE_2 and ΔE_3 (eV) and transition temperatures T_s (°C) for the investigated ligands and their metal complexes

Compounds ^a	$\log \sigma$	ΔE_1	ΔE_2	ΔE_3	T_s
I	-11.35	0.186	2.723		65
[FeLCl ₂ (OC ₂ H ₆)]·H ₂ O	-9.35	0.329			
[CoLCl(H ₂ O)]·H ₂ O	-11.30	0.380			
[CuLCl(H ₂ O)]	-11.275	0.379			
[CuL(Ac)(H ₂ O)]·H ₂ O	-12.46	0.096	0.455		79
[NiLCl(H ₂ O)]·H ₂ O	-10.78	0.618			
II	-13.075	0.043	0.778		100
[FeL̄Cl ₂ (H ₂ O) ₂]·H ₂ O	-7.075				
[CoL̄ ₂ Cl]·3H ₂ O	-11.925	0.445			
[CuL̄ ₂ Cl]·H ₂ O	-11.20	0.9519			
[CuL̄Ac(H ₂ O)]·C ₂ H ₅ OH	-13.10	0.096	0.368		76
[Ni(HL̄)Cl ₂]·H ₂ O	-11.90	0.147			
[MnL̄ ₂]·H ₂ O	-12.375	0.495			
III	-11.425	0.700	0.099	1.206	62, 90
[FeL̄Cl ₂ (H ₂ O) ₂]·H ₂ O	-9.50	0.535	0.149		48
[CuL̄(H ₂ O)]·H ₂ O	-12.125	0.082	0.528		74
[CuL̄(Ac)(H ₂ O)]·H ₂ O	-12.22	0.582	1.683		74
[Ni(HL̄)Cl ₂]	-10.75	0.511			

^a HL, HL̄ and HL̄ denote the ligands **I**, **II** and **III**, respectively.

pressure of 300 kg cm^{-2} . The measurements were carried out in air in the temperature range $28\text{--}150^\circ\text{C}$ using a super Megohmmeter electrometer (Model RM 170). Good contact of the electrodes with the surfaces of the disc was obtained by carefully painting the surfaces with silver paste. The temperatures of the samples were measured using a digital thermometer placed close to the sample. The conductivity σ of the samples was obtained on heating using the equation $\sigma = 1/R \times d/A$, where R is the resistance and d and A are the thickness and the cross sectional area of the powder disc, respectively.

The measurements of current (I) for a series of applied voltages (V) of the ligands and some of the metal complexes were obtained at $10 < V < 450$ volts.

RESULTS AND DISCUSSION

The variations of the electrical conductivity ($\log \sigma$) with the reciprocal temperature ($1000/T$) of the ligands and their metal complexes are shown in Figs. 1, 2 and 3. The conductivity-temperature dependence satisfies the known equation

$$\sigma = \sigma_0 \exp(-\Delta E/KT)$$

where σ_0 is a constant (pre-exponential factor), ΔE is the activation energy and K is the Boltzmann constant. It can be shown that there is a positive coefficient of the electrical conductivity ($d\sigma/dT$) for all samples under investigation. Therefore they possess semiconducting properties.

The electrical conductivity-temperature curves for metal-free ligands **I** and **II** show a discontinuity at transition temperatures (T_s) of 65 and 100°C respectively. Hence these ligands have two activation energy values (ΔE_1 and ΔE_2). However, the conductivity curve for ligand **III** shows two breaks at transition temperatures of 62 and 90°C and therefore this ligand has three activation energies (ΔE_1 , ΔE_2 and ΔE_3). The ΔE and T_s values and the magnitudes of conductivity ($\log \sigma$) at 30°C have been deduced, and are listed in Table 1. It can be seen that the activation energy values of ligand **II** are lower than the corresponding values of ligands **I** and **III**. In contrast, the conductivity at 30°C of ligand **II** is lower than that of ligands **I** and **III**. It has been established that anisotropy [4], pressure [5], temperature [2] and structure [6] affect the conductivity and/or the activation energy. In addition, it is quite common to find a low ΔE value associated with a relatively high resistivity [2,7]. In the present context, it would be reasonable to suggest that ΔE and σ are associated with the temperature as well as the substituent on the benzene ring. The variation in the strength of hydrogen bond formation between the anil and the OH groups plays a role in the delocalization of charge carriers and hence affects the ΔE and σ values.

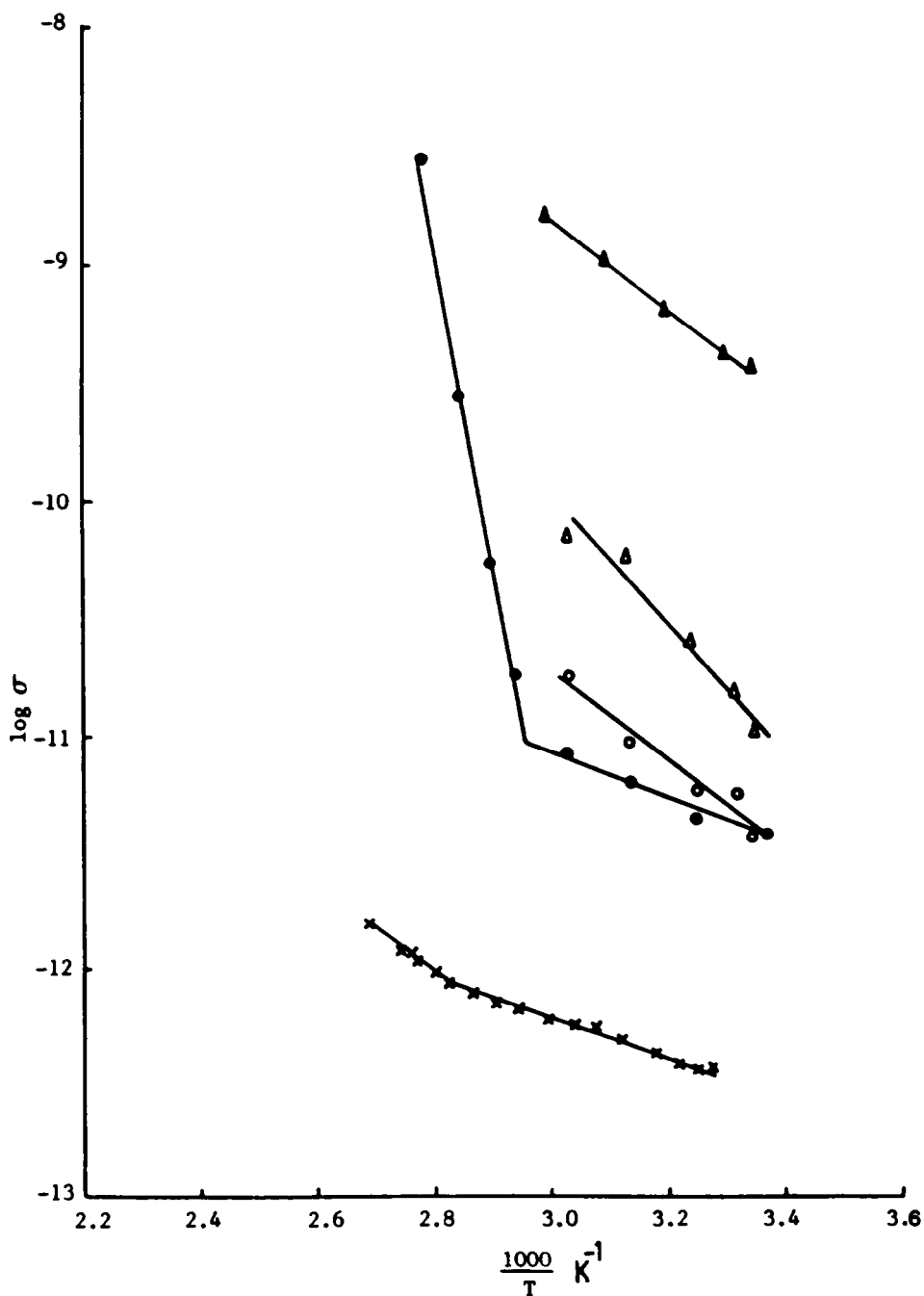


Fig. 1. $\log \sigma$ vs. $1/T$ relationships of ligand I (●), its metal chloride complexes Cu (○), Ni (△), Fe (▲); and its copper acetate complex (×).

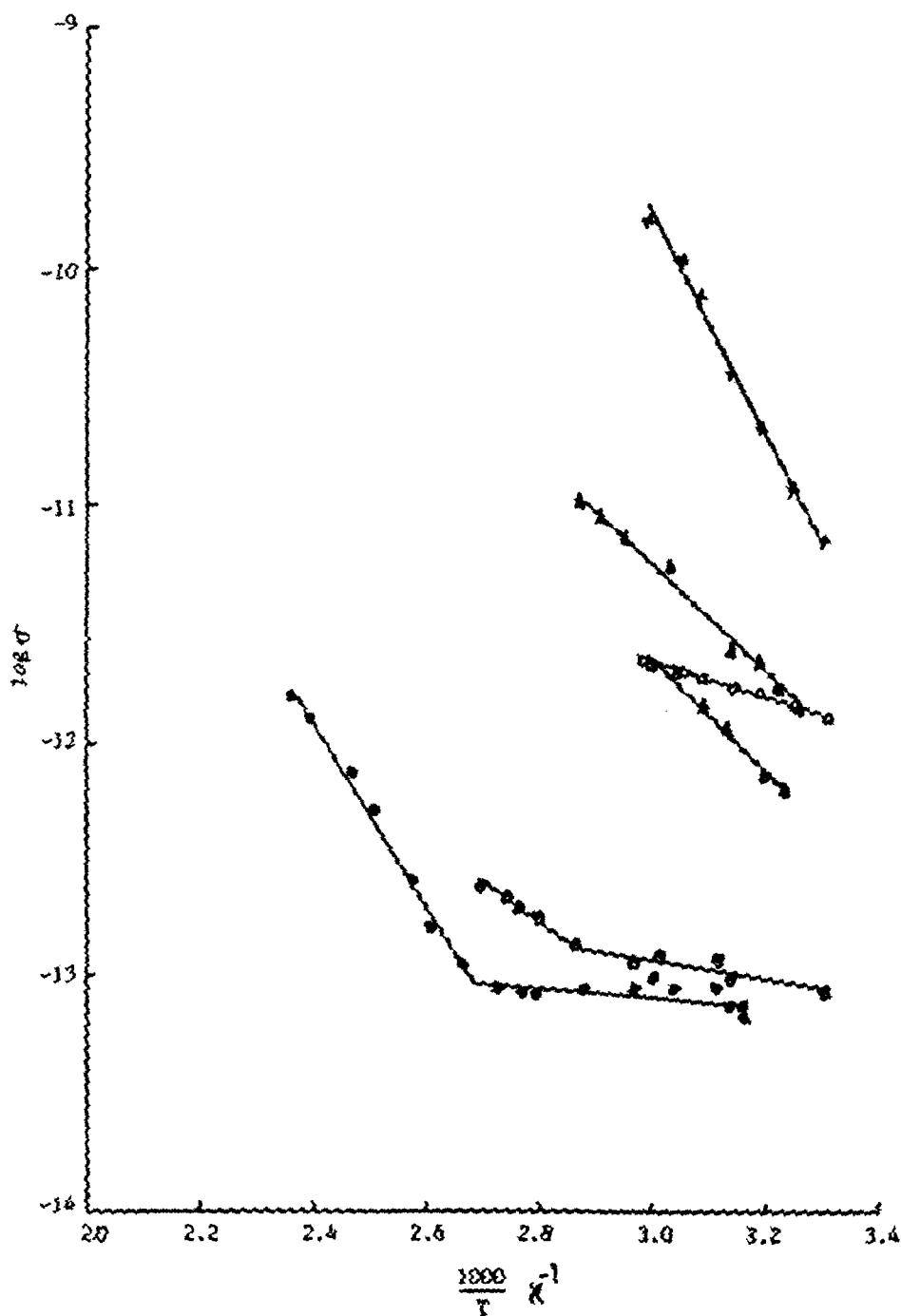


Fig. 2. $\log \sigma$ vs. $1/T$ relationships of ligand II (●), its metal chloride complexes Cu (×), Ni (○), Co (▲), Mn (△), and its copper acetate complex (⊙).

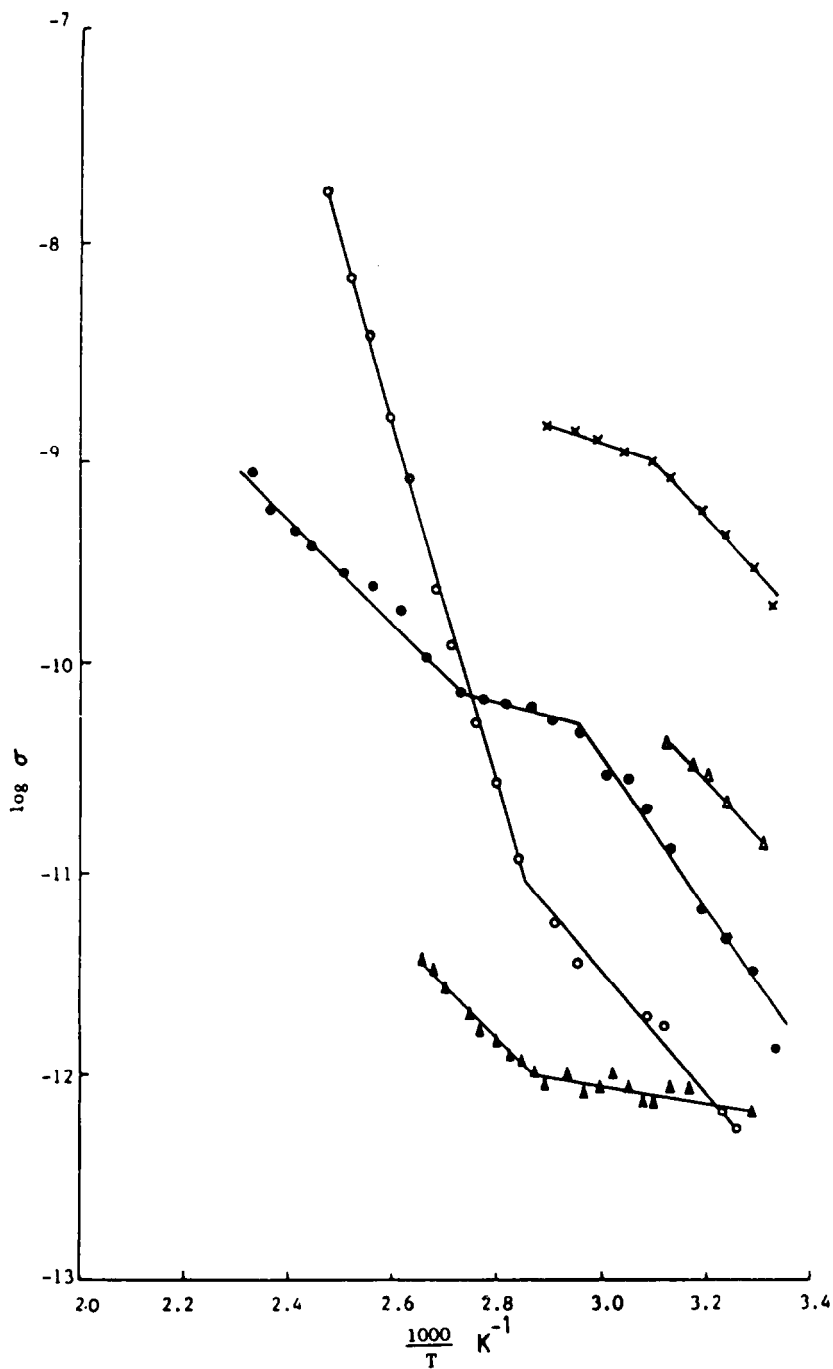


Fig. 3. $\log \sigma$ vs. $1/T$ relationships of ligand III (●), its metal chloride complexes Cu (▲), Ni (△), Fe (×); and copper acetate complex (○).

Concerning the electrical properties of the metal chloride complexes, it is worth noting the finding that the σ and ΔE values of the ligands are affected on complexation. The conductivities of the metal complexes are, on the whole, significantly lower than those of the metal-free compounds; see Figs 1, 2 and 3 and Table 1. This has been ascribed to increases in mobility consequent upon the replacement of the hydrogens with a metal ion to form new molecular orbitals (MO) which are delocalized over the whole complex. Such overlap may arise from excitation of a compound to the triplet state or by some other force, possibly charge transfer, hydrogen bonding or any resonating interactions encountered in the organic structures [8,9]. According to this mechanism, the introduction of the metal ions will affect ΔE and σ if the ions affect the mechanism by which MO overlap takes place. As can be seen from Table 1, the magnitudes of ΔE and σ indicate slight semiconducting properties, hence the electron delocalization is not of high mobility.

The conductivity at 30°C of the complexes with ligand **II** follows the order $\text{Fe} > \text{Cu} > \text{Ni} \approx \text{Co} > \text{Mn}$. However the relevant order for ligands **I** and **III** is $\text{Fe} > \text{Ni} > \text{Cu} \approx \text{Co}$ and $\text{Fe} > \text{Ni} > \text{Cu}$. It has been suggested that the conductivity depends on the ionic radius of the cation ($r(\text{\AA})$) as well as the stability of the complex [2,9]. Figure 4 illustrates that $\log \sigma$ increases with decreasing radius r of the cation ($\text{Mn}^{2+} = 0.8$, $\text{Co}^{2+} = 0.72$, $\text{Cu}^{2+} = 0.72$, $\text{Ni}^{2+} = 0.69$ and $\text{Fe}^{3+} = 0.53 \text{\AA}$) [10]. The correlation coefficients (R) for the linear regression $\log \sigma$ vs. r of the metal complexes with ligands **I** and **II** are 0.995 and 0.941 respectively. The deficiency of data points in the case of ligand **III** makes this linear regression unreliable.

Electrical measurements were made for complexes of copper acetate with different ligands; see Figs. 1, 2 and 3. The conductivity-temperature curves show two modes of conduction at transition temperatures in the range 74–79°C. The values of ΔE , $\log \sigma$ at 30°C and T_s are listed in Table 1. It can be shown that these complexes all exhibit lower conductivity than the corresponding copper chloride complexes or the free ligands. This finding could be attributed to the inductive effect of the acetate group, which could decrease the delocalization of the charge carriers towards the ligand. The discontinuity observed in the conductivity-temperature curves of the metal-free ligands as well as some of the metal complexes could be ascribed to a change in type of packing, a volume change or to crystallographic transitions [11,12].

The I - V data for different ligands were measured at different temperatures and were plotted on the log-log scale; Fig. 5 shows these plots for the metal-free ligand **II**. The values of n and the ranges of applied voltage for different ligands are listed in Table 2. It can be seen that the dependence $I \propto V^n$ is linear with $n \approx 1$. Hence it is concluded that these ligands obey Ohm's law, which is temperature independent. The same measurements were carried out for the metal chloride complexes with ligand **II** (Table 2).

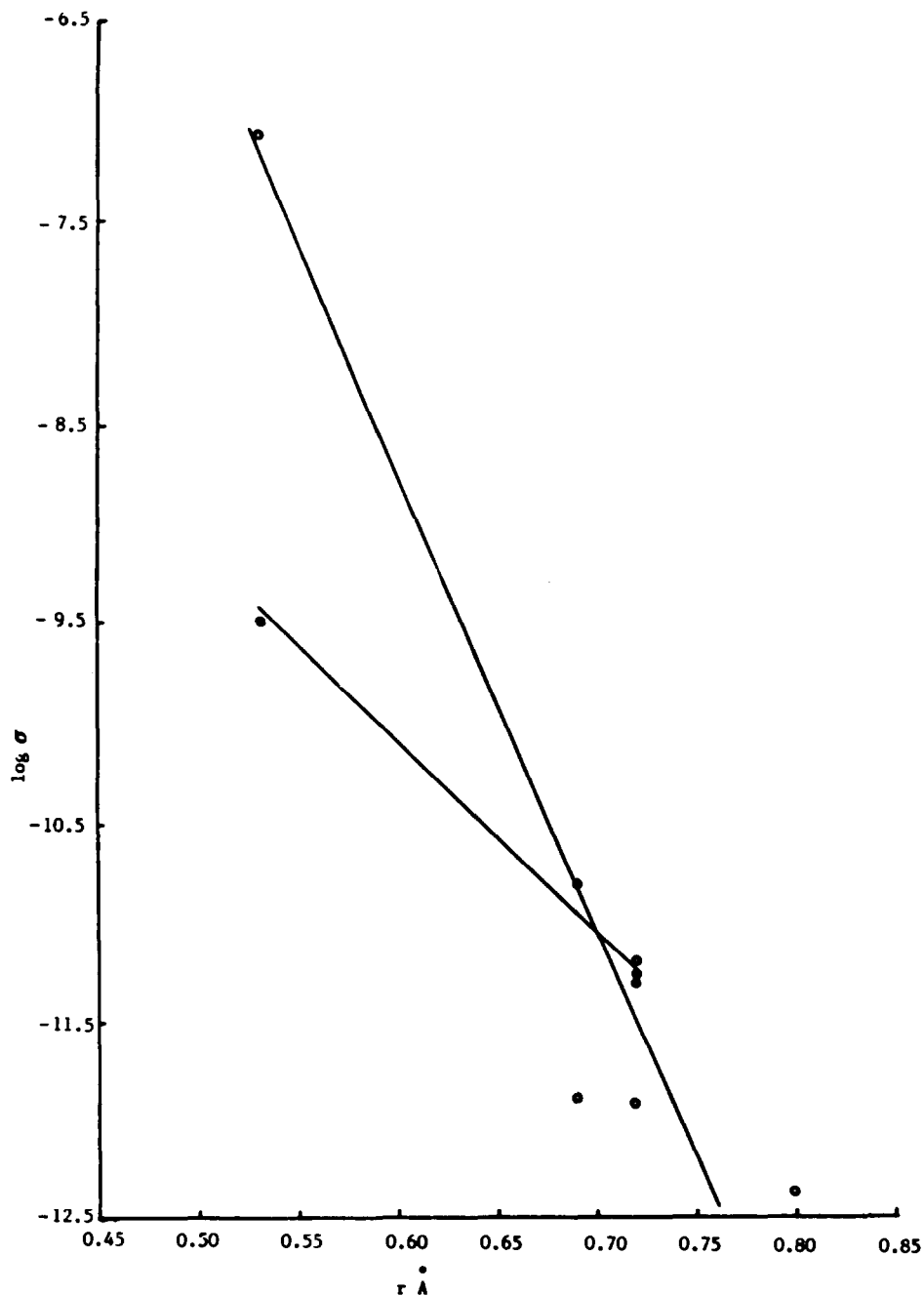


Fig. 4. $\log \sigma$ vs. r (Å) relationships of the metal chloride complexes with ligand I (●) and ligand II (○).

This revealed that the Mn and Ni complexes have ohmic conduction with $n = 1.045$ and 0.971 , respectively, in the range of applied voltages $10 < V < 300$. However, the plots for the Cu and Co complexes (Fig. 5) at $60 < V <$

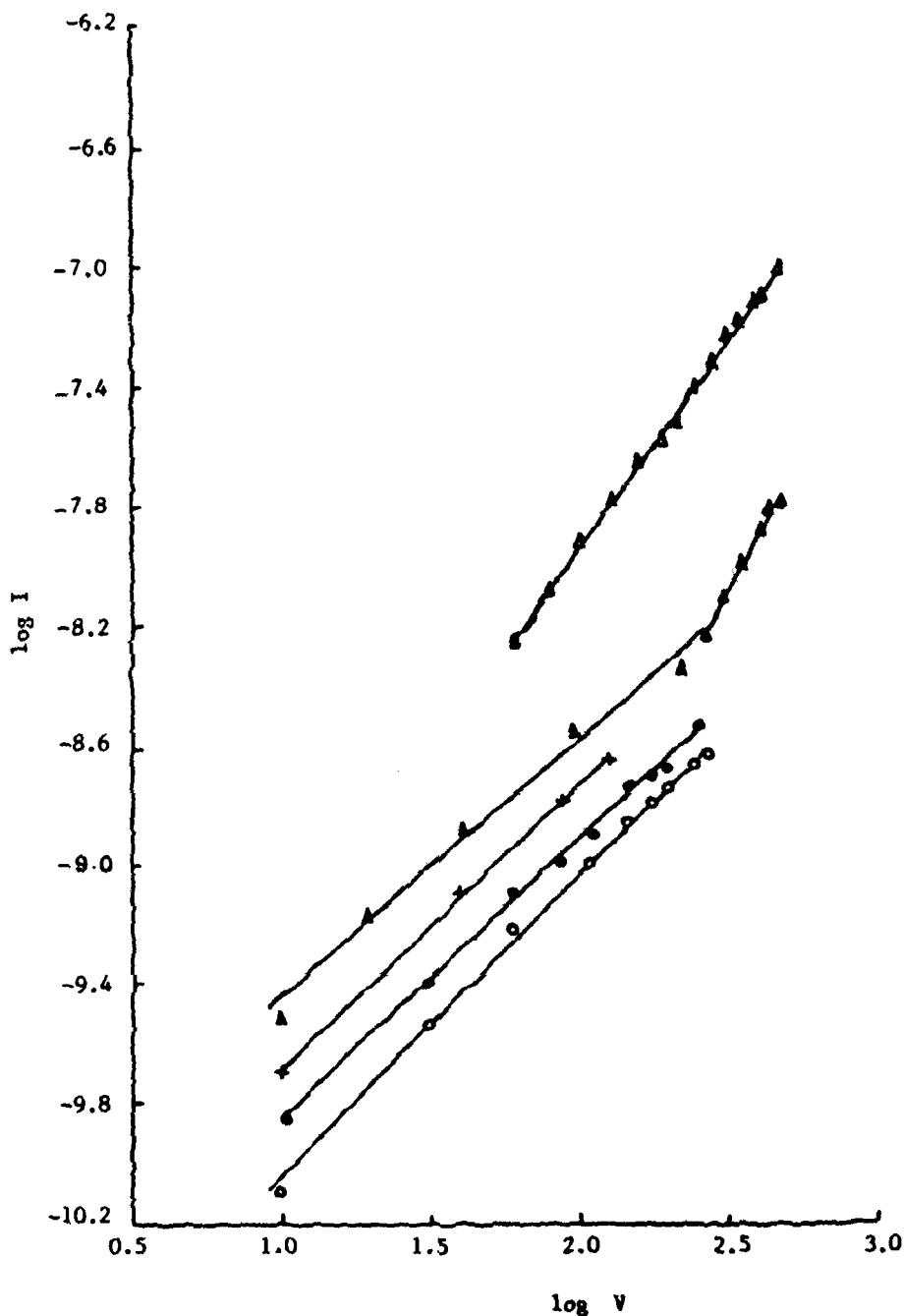


Fig. 5. $\log V$ vs. $\log I$ plots of ligand II at 31°C (●), 65°C (○) and 145°C (×); and its copper (△) and cobalt (▲) complexes, respectively.

TABLE 2

The values of n and the correlation coefficient (R) at different ranges of applied voltage (V) and temperature ($^{\circ}\text{C}$) of the ligands and some of their metal complexes

Compound	Applied voltage	Temp.	n	R
I	10–160	25	0.909	0.998
	10–330	70	1.044	0.996
II	10–250	31	0.925	0.998
	10–280	65	1.043	0.997
	10–130	145	0.958	0.999
III	10–140	30	0.969	0.998
	10–150	60	1.005	0.992
	10–340	140	1.083	0.999
$[\text{Mn}\bar{\text{L}}_2] \cdot \text{H}_2\text{O}$	10–300	37	1.045	0.992
$[\text{Ni}(\text{HL})\text{Cl}_2] \cdot \text{H}_2\text{O}$	10–270	31	0.971	0.997
$[\text{Cu}\bar{\text{L}}_2\text{Cl}] \cdot \text{H}_2\text{O}$	60–490	33	1.379	0.996
$[\text{Co}\bar{\text{L}}_2\text{Cl}] \cdot 3\text{H}_2\text{O}$	10–230	36	0.886	0.987
	230–480		1.914	0.997
$[\text{NiLC}(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$	10–100	33	2.180	0.990
	100–490		1.359	0.997
$[\text{Ni}(\text{HL})\text{Cl}_2]$	10–340	41	0.961	0.960

490 and $10 < V < 230$ show nearly ohmic behaviour. For the Co complex at higher applied voltages up to 480 V, the data fit the $\log I$ – $\log V$ dependence with $n = 1.914$, suggesting that this complex in this range of applied voltages exhibits space charge limited current (SCLC) conduction [13].

The I – V data for Ni complexes with ligands **I** and **III**, in the range of applied voltages $10 < V < 100$ and $10 < V < 340$ fit the proportionality $I \propto V^n$ with $n = 2.18$ and 0.961 respectively. However, a value of $n = 1.359$ was obtained for the first complex in the range of applied voltages from 100 up to 490. Hence the Ni complex with ligand **I** proceeds from SCLC to nearly ohmic conduction, whereas the Ni complex with ligand **III** over all the range of applied voltages obeys Ohm's law.

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