Thermochimica Acta, 156 (1989) 225–230
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CONDUCTING PROPERTIES OF SOME NEW AZO-NITROSO COMPLEXES

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(Received 23 March 1989)

ABSTRACT

Electrical conductivity measurements of some transition metal complexes of chelators derived from *p*-substituted phenylazo-2,4-dinitrosoresorcinol were investigated in the temperature range 30–370 ° C. The results indicated slight semiconducting behaviour. The mobilities were calculated and the hopping model was applied to explain the conducting process.

INTRODUCTION

Throughout the literature, there are many papers concerning the chemistry of azo and nitroso compounds. The major areas of interest lie in diverse fields: structural, analytical, chemotherapy, dyeing, etc. Recently, a few papers have appeared concerning the conducting properties of azo and nitroso compounds [1–6]. This is the first paper in a series concerning the conducting properties of complexes containing both azo and nitroso functional groups. It is demonstrated that the conductivity data are related to their physicochemical properties.

EXPERIMENTAL

The organic compounds, namely *p*-substituted phenylazo-2,4-dinitrosoresorcinol, were synthesized in two steps: resorcinol was nitrosated to form 2,4-dinitrosoresorcinol; and the amine was diazotized and coupled with

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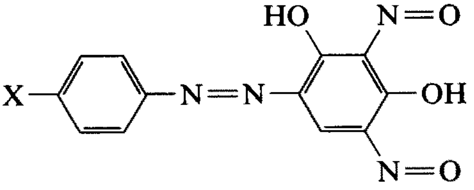
the prepared nitroso compound. The general structural formula for these compounds is given below.



X = H, NO_2, CH_3 or $-OCH_3$.

The solid complexes were prepared by mixing the required weights of the metal salts with the corresponding ligand in aqueous alcoholic media. The compounds formed were filtered, washed several times with alcohol and dried in a vacuum desiccator over P_4O_{10}. The analytical data for the complexes gave the following results: for the –H ligand, the complexes FeL_3, $CoL_2 \cdot 2H_2O$, $NiLCl_2$ and $CuL \cdot Cl_2 \cdot 2H_2O$ were formed; the $-NO_2$ complexes were FeL_3, $Co_2L_3 \cdot 2H_2O$, $NiL \cdot Cl \cdot H_2O$ and $CuL \cdot Cl$; the $-OCH_3$ ligand gave FeL_3, Co_2L_3, $NiL \cdot 2H_2O$ and CuL complexes; and the $-CH_3$ complexes were FeL_3, $CoL_2 \cdot H_2O$, $NiL \cdot Cl \cdot H_2O$ and $CuL \cdot Cl$.

For the electrical conductivity measurements, the samples were prepared in the form of tablets of 1 mm thickness at a pressure of 2000 kg cm^{-2}. The samples were held between two copper electrodes and were then inserted with the holder vertically into a cylindrical electric furnace. The potential across the heater was varied gradually using a Variac transformer. This produces the slow rate of temperature increase required to obtain accurate measurements. The electrical measuring circuit consisted of an audio frequency R.C. oscillater type TR-0101-F and a millivoltmeter BM 384 Tesla. The temperature of the sample was measured to within ±0.1°C by means of a copper–constantan thermocouple.

RESULTS AND DISCUSSION

Of all the solids that have technical application, semiconductors are among the most interesting. Electronic devices, mainly the transistor, are made from semiconductors. In the power field, semiconductor rectifiers have largely replaced the mercury arc rectifier and semiconductor devices can be used to effect commutation in rotating machines. Silicon-controlled rectifiers are becoming widely used in control applications and semiconductor thermoelectric generators and refrigerators are being made.

The conductivity measurements of all the complexes under investigation were obtained in the solid state using pressed pellets over the temperature range 30–370°C. The dependence of the conductivity of semiconducting

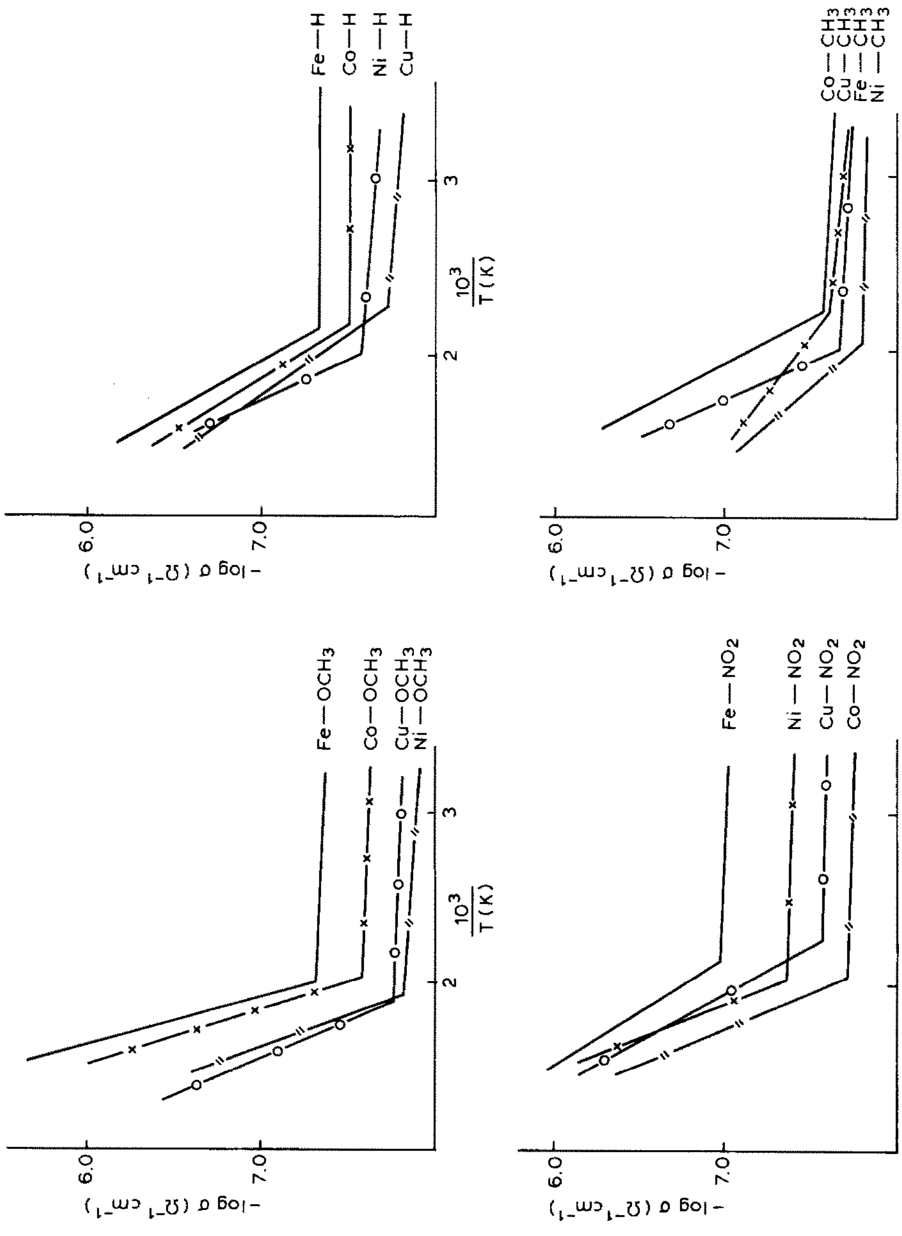


Fig. 1. −log σ versus $1/T$ for metal complexes of *p*-substituted phenylazo-2,4-dinitroresorcinol.

TABLE 1

Conductivity data of *p*-substituted phenylazo-2,4-dinitrosoresorcinol complexes [a]

Compound	ΔE	$-\log \sigma_0$
$X = -H$		
FeL_3	0.69	3.3
$CoL_2 \cdot 2H_2O$	0.66	3.9
$NiL \cdot Cl_2$	0.78	3.4
$CuL \cdot Cl_2 \cdot 2H_2O$	0.59	4.4
$X = -CH_3$		
FeL_3	0.89	2.8
$CoL_2 \cdot H_2O$	0.75	3.3
$NiL \cdot Cl \cdot H_2O$	0.46	5.4
$CuL \cdot Cl$	0.33	5.8
$X = -OCH_3$		
FeL_3	1.6	1.0
$Co_2L_3 \cdot 2H_2O$	1.23	1.6
$NiL \cdot Cl \cdot H_2O$	0.99	3.1
$CuL \cdot Cl \cdot H_2O$	0.85	3.5
$X = -NO_2$		
FeL_3	0.78	3.6
$Co_2L_3 \cdot 2H_2O$	0.99	2.8
$NiL \cdot Cl \cdot H_2O$	1.09	2.5
$CuL \cdot Cl$	0.85	3.5

[a] The ligands take the symbol H_2L.

materials on temperature is expressed by the equation [7] $\sigma = \sigma_{0e}^{-E_a/KT}$ where E_a is the activation energy for conduction and σ_0 is the specific conductivity as defined by $\sigma_0 = \sigma_{(T \to \infty)}$. The electrical conductivity data (ΔE, $-\log \sigma_0$) (see Fig. 1) are collected in Table 1. All the complexes follow the same trend: the $-\log \sigma$ values decrease with temperature increase until there is a sharp break following which the conductivity values are virtually constant irrespective of the change in temperature. All the prepared complexes had low activation energy values, i.e. they have faint semiconducting properties. Hence, the electrons in the available orbitals of the complexes are not of high mobility. The complexes with $-NO_2$ and $-OCH_3$ substituents have large ΔE values with respect to the complexes without any substituent ($-H$). So the presence of these substituents renders the compounds more conducting. However, the metal complexes of $-H$, $-CH_3$ and $-OCH_3$ substituent ligands show a remarkable effect in which as the atomic number of the metal increases, the activation energy decreases, and the $-\log \sigma_0$ values increase. This indicates that the presence of holes in the system has little effect on the mobility of charges [3].

The mobilities μ of the complexes were calculated from the equation $\sigma = eN_0^{\mu}$ using the value of $N_0 = 10^{21}$. The values of μ were in the range

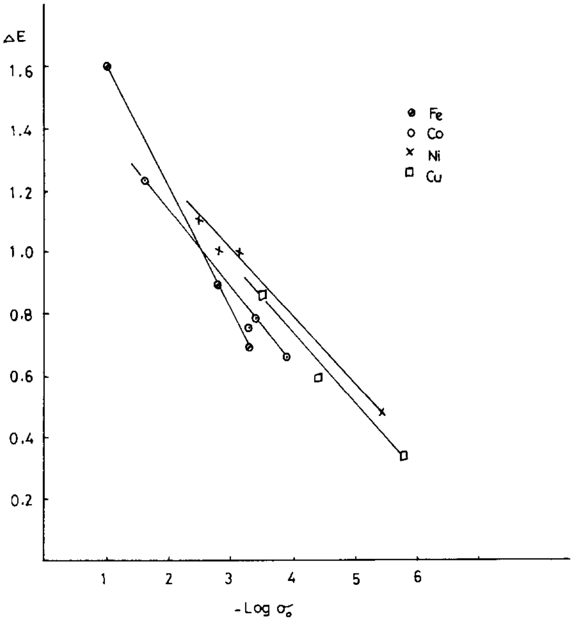


Fig. 2. ΔE versus log σ_0 for metal complexes of *p*-substituted phenylazo-2,4-dinitrosoresorcinol.

10^{-8}–10^{-10} $cm^2\ V^{-1}\ s^{-1}$. The fact that these values are much smaller than 1 $cm^2\ V^{-1}\ s^{-1}$ can be used as a criterion for applying the hopping model for the description of the mechanism of conductance. Therefore the charge carrier passes to another molecule over the top of the barrier via an excited state. The most realistic description of the complexes involves an interaction of the metal orbitals with ligands to give new molecular orbitals (MO), which are delocalized over the whole molecular complex [8]. It has been proposed [9] that the first step in the conduction process is the excitation of the π-electron from the uppermost filled π-orbital to the lowest empty π-MO. The electron is then assumed to transfer to the equivalent empty level of the neighbouring molecule. In most complexes, during thermal agitation an additional increase in electrical conductivity occurs, probably indicating a discontinuity of the chemical bonds existing in the compounds. This is a useful criterion for ascertaining the nature of the metal–ligand bonding. However, if the ΔE values are correlated with the Hammett constants, σ, scattered lines are obtained; thus, the activation energy values are affected by the electronic requirements of the substituents but the trend is irregular.

Figure 2 represents the relation between ΔE and $-\log \sigma_0$ values. Straight lines were obtained for the systems under investigation. Empirical equations were constructed to correlate these two parameters as follows: for the iron complexes, $\Delta E = 0.4 \log \sigma_0 + 2.0$; for the cobalt complexes, $\Delta E = 0.27 \log \sigma_0 + 1.64$; for the nickel complexes, $\Delta E = 0.22 \log \sigma_0 + 1.64$; and for the copper complexes, $\Delta E = 0.24 \log \sigma_0 + 1.64$.

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