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FURTHER STUDIES ON THE TEMPERATURE DEPENDENCE OF ELECTRICAL AND SEMICONDUCTING PROPERTIES OF Co(II), Ni(II) AND Cu(II) COMPLEXES OF MERCAPTOBENZOTHIAZOLE SINGLE CRYSTALS

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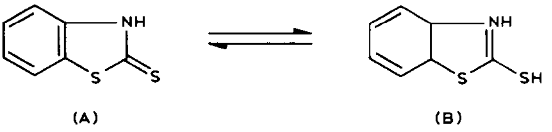
ABSTRACT

The present investigation aims to evaluate the mechanism of electrical conductivity of single crystals of mercaptobenzothiazole and its Co(II), Ni(II) and Cu(II) complexes in the temperature range 295–420 K and to relate the mechanism to the physicochemical properties of these complexes, a study not previously recorded in the literature. In this respect, mercaptobenzothiazole (MBTH) and its Co(II), Ni(II) and Cu(II) complexes were synthesized and prepared for the first time in the form of single crystals. From results obtained, it was found that the materials possess semiconducting properties in the investigated temperature range. On going from Co(II) or Ni(II) complexes to Cu(II) complexes, the electrical conductivity increased and the activation energy decreased from 2.4 eV down to 0.85 eV. This was attributed to the formation of a bridge between the two ligand molecules and the metal ion, thus facilitating the transfer of current together with the increased number of *d*-electrons and the formation of a conjugated polymer in the same direction.

INTRODUCTION

It is of importance to note that 2-mercaptobenzothiazole (MBTH) and its metal complexes find great industrial applications. MBTH is used for the volcanization of rubber [1], against chemical corrosion [2] and in medicine [3,4].

MBTH is a thiocarbenyl derivative which can be represented by two tautomeric forms: thioketone (A) and thioenol (B)



Spectral studies showed that the presence of the –NH–C=S group exists in the solid form and the ligand exists mainly in the thioketone form (A) [5,6].

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The greater interest [7–10] in the electron transport character of organic crystals, charge transfer in complexes, coordination compounds and radical anion salts has enhanced this report on the results of evaluating the mechanism of electrical conduction of mercaptobenzothiazole ligand chelates. The conducting properties of organic compounds usually correlate with the energy difference between the highest occupied and the lowest empty molecular orbitals, suggesting that the transportation of electrons in these systems involves the non-bonding/empty molecular orbitals of the compounds.

The aim of the present investigation is to throw light on the mechanism of electrical conduction of single crystals of mercaptobenzothiazole ligand and its Co(II), Ni(II) and Cu(II) solid complexes, in correlation with their physicochemical properties. Such a study has not been tackled before.

MATERIALS AND METHODS

Starting materials and sample preparation

The pure chemical 2-mercaptobenzothiazole available was recrystallized from absolute ethyl alcohol several times. The product was dried thoroughly over P_2O_5 for one week, to constant weight.

The solid metal complexes were prepared by mixing the corresponding required weights of the metal chlorides and the ligand in ethanolic media. The complexes formed were digested on a water bath, cooled, filtered off and washed with a hot mixture of ethanol and ether. The complex was dried in a vacuum desiccator over P_2O_5. The complexes obtained could not be crystallized since they are practically insoluble in any of the organic solvents available at present. Single crystals, 0.5 mm thick and 5 mm long, were carefully prepared from both MBTH ligand and its transition metal complexes by evaporation/condensation and melting techniques under vacuum (10^{-4} mm Hg).

The preparation, chemical analysis and melting point determinations of all the prepared complexes were undertaken and recorded in Table 1.

TABLE 1

Chemical analysis, melting point and decomposition points of the prepared solid metal complexes

Chemical formula	Metal (wt.%)		Decomposition point (°C)	Melting point (°C)	Colour
	Calc.	Found			
Co(MBT·Cl)	22.7	22.66	201	–	Brown
$Ni(MBT)_2$	15.01	15.00	303	–	Dark green
$Cu(MBT)_2$	16.00	16.10	–	199	Yellow

Thermogravimetric analysis (TGA)

All samples were analysed thermogravimetrically using an automatic recording thermobalance (Gebr. Netzsch, Selb, F.R.G.) in which the temperatures were recorded automatically as a function of weight in the range 20–150°C. This was done to detect the stability zone of the investigated materials for subsequent measurements.

d.c. Electrical conductivity measurements versus temperature

For measurements of electrical conductivity, the prepared single crystals were carefully handled between two copper electrodes and the d.c. current was allowed to pass in the direction of the long axis of the single crystals. This is due to difficulties in measuring across the single crystals, i.e., in the direction of the short axis. This was undertaken and evaluated using a (Va-J-51) electrometer with a d.c. power of 0–100 V (supplied from a series of dry batteries). Copper electrodes and silver contacts were set up. The temperature of the furnace was recorded throughout the run by means of a copper–constantan thermocouple.

The above measurements were repeated several times on fresh dried specimens in order to attain reproducible data.

RESULTS AND DISCUSSION

Chemical analysis indicates the correct stoichiometry of the prepared solid metal complexes.

Thermogravimetric measurements reveal that there are no weight changes for all the investigated materials, indicating a stable temperature range from 20 to 150°C for subsequent measurements of electrical conductivity.

The variation of log σ (σ = electrical conductivity) of the MBT ligand and its metal complexes with the reciprocal of the absolute temperature ($1000/T$ K^{-1}) in the temperature range 18–150°C gave straight lines (Fig. 1), indicating semiconducting character rather than metallic conductivity [11], and the promotion of electrons from the ground to the excited states may be necessary before conduction occurs [12].

It has been assumed that the first step in the conduction process is the excitation of electrons from the highest filled molecular orbitals to the lowest π molecular orbitals. Thus, an electron is assumed to tunnel to the equivalent empty level of the neighbouring molecule in the anodic direction whereas a positive hole moves to a molecule in the cathodic direction.

In this investigation, the electrical conductivity (σ) values can be represented by an equation of the form

$$\sigma = \sigma_0 \exp(-\Delta E/KT) \qquad (1)$$

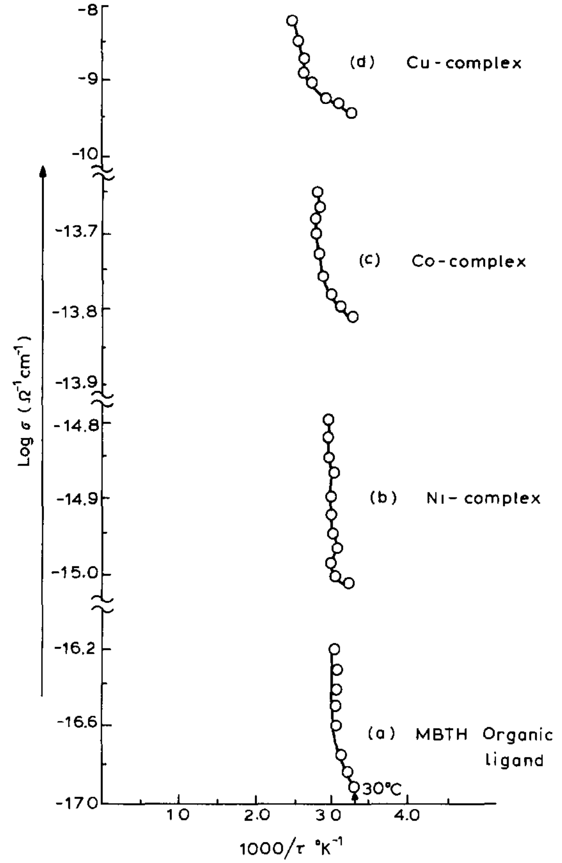

Fig. 1. A schematical diagram indicating the temperature dependence of the electrical conductivity of: (a) MBTH ligand, (b) Ni(MBT)$_2$, (c) Co(MBT·Cl) and (d) Cu(MBT)$_2$.

where σ_0 is a constant independent of temperature, K is the Boltzmann constant and ΔE is the activation energy. The results obtained are recorded in Table 2.

Based on the insolubility of these metal complexes, interaction might occur between adjacent atoms in a metal-atom chain. Indeed, the "metal

TABLE 2

The semiconducting parameters of MBTH ligand and its transition metal complexes

Compound	No. of *d*-electrons	Log σ_{30}	ΔE (eV)	Energy gap, E_g (eV)
MBTH	0.0	−16.95	2.4	4.80
Co(MBT·Cl)	7.0	−13.80	1.8	3.60
Ni(MBT)$_2$	8.0	−15.20	1.9	3.80
Cu(MBT)$_2$	9.0	−9.60	0.85	1.70

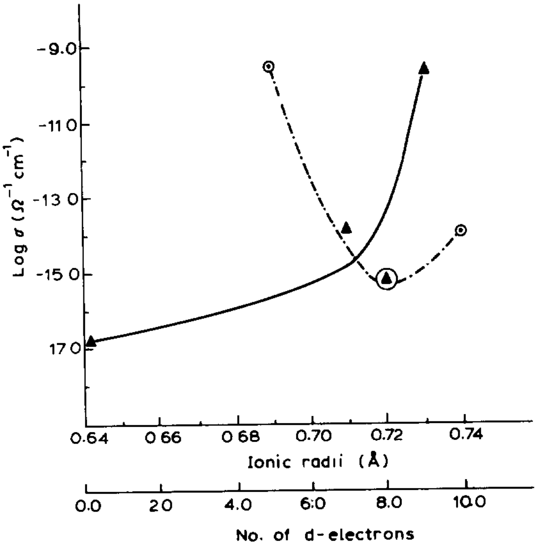

Fig. 2. Variation of log σ_{30} as a function of: (○) ionic radii (Å) of the transition metal ions, (▲) number of *d*-electrons of the transition metal ions.

chain complexes" have been a topic of considerable interest recently [13–18].

The ΔE value for MBTH was found to be 2.40 eV. The room temperature specific conductivity, log σ_{30} (°C), is equal to 16.95 (Ω^{-1} cm^{-1}). During thermal agitation an additional increase of electrical conductivity occurs, probably predicting a discontinuity of the chemical bonds existing in the compounds.

The higher electrical conductivity and lower activation energy obtained for Co(II) complexes (1.8 eV) than for Ni(II) complexes (1.9 eV) may be attributed to the higher metallic proportion in the former (see Chemical Analysis, Table 1). However, on going from the ligand, Co(II) or Ni(II) through to Cu(II) complexes, a decrease in the activation energy and an increase in the specific conductivity occurs (see Figs. 1–3). Fortunately, the results given in Figs. 1–3 hold good and support each other.

Accordingly, it was assumed that the metal ion acts as a bridge between the two ligands, thus facilitating the transfer of current carriers during measurements, leading to an increase in the electrical conduction and a decrease in the activation energy. On the other hand, this mechanism indicates the possibility of some degree of delocalization in the excited state, but little or none could be expected in the ground state.

Finally, the relatively low activation energy for the Cu(II) complex (0.85 eV) compared with the other complexes is due to the existence of one more *d*-electron for the Cu(II) ion than for the others; these electrons will occupy the dx^2-y^2 orbitals and will be likely, therefore, to take part in intermetallic interactions leading to a noticeable increase in electrical conductiv-

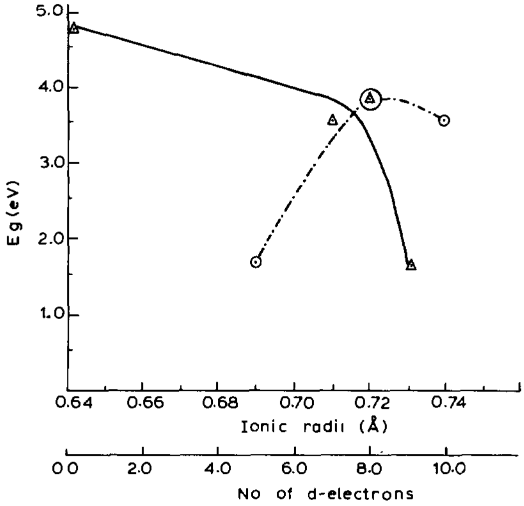

Fig. 3. Variation of the energy gap, E_g (eV), as a function of: (O) ionic radii (Å) of the transition metal ions, (△) number of *d*-electrons of the transition metal ions.

ity and a decrease in activation energy. Moreover, the Cu(II) complex was found to be polymeric in nature [16], leading to the pronounced high conductivity. Figure 2 shows the variation of log σ_{30} as a function of both the number of *d*-electrons and the ionic radii of the transition metal ions. Figure 3 shows the variation of E_g as a function of the number of *d*-electrons and the ionic radii of the transition metal ions. It can be easily seen that these relationships are in conformity and hold good.

This directional character of the electrical conductivity was in good conformity with that previously noted for Na- and K-acetyl acetonates [19,20].

From Figs. 2 and 3, it was concluded that the conductivity (log σ_{30}) increases whereas ΔE and E_g decrease on going from Co(II) to Cu(II) solid complexes of mercaptobenzothiazole (Figs. 2 and 3). This observation could be ascribed to the increased number of valence electrons (*d*-electrons) and/or the polymeric nature of the Cu(II) complex. This may facilitate the flow of electric current in the same direction.

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