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THERMAL STUDIES ON THE ELECTRICAL CONDUCTIVITY OF SOME $(C_nH_{2n+1}NH_3)_2CuCl_4$ ($n = 1,2$) AND $(CH_2)_2(CH_3)_2CuCl_4$ COMPLEXES

M.A. AHMED

Physics Department, Faculty of Science, Cairo University, Giza (Egypt)

M.A. ABD EL-KAFFAR

Polymer and Pigments Laboratory, National Research Centre, Cairo (Egypt)

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ABSTRACT

The electrical conductivities of the compounds $(CH_3NH_3)_2CuCl_4$, $(C_2H_5NH_3)_2CuCl_4$ and $(CH_2)_2(NH_3)_2CuCl_4$ were measured in the temperature range which includes their structural phase transition. The values of the activation energies as calculated from the Arrhenius equation are reported. Confirmation of the phase transition temperatures is carried out using differential thermal analysis in the same temperature range as the conductivity measurements.

INTRODUCTION

The two compounds $(CH_3NH_3)_2CuCl_4$ and $(C_2H_5NH_3)_2CuCl_4$, indicated below $(MeA)_2CuCl_4$ and $(EA)_2CuCl_4$, are two members of the series $(C_nH_{2n+1}NH_3)_2CuCl_4$. This series of compounds has been extensively studied by de Jong and Miedema [1]. It consists of nearly quadratic layers of metal ions which are surrounded by halogen sharing octahedral corners within the layer. The layers are widely separated by non-magnetic alkylammonium groups. The compound $(CH_2)_2(NH_3)_2CuCl_4$ consists, as in the first series, of a two-dimensional array, but the difference is in the replacement of the alkylammonium group by the alkylene ammonium group. Also, the adjacent layers are shifted in relation to each other in such a way that the Cu^{2+} ions lie on the top of each other.

For some organic compounds containing a hydrogen bond [2], it is necessary to consider the possibility of the existence of the intrinsic conductivity. In this case, electrical conductivity is established by the protons of the hydrogen bond through a hole mechanism. The conductivity of the compounds under investigation is mainly discussed from this point of view.

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TABLE 1

Chemical analysis

Compound	C(%)		H(%)		N(%)		Cl(%)		Cu(%)	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
$(MeA)_2CuCl_4$	8.75	8.91	4.40	4.45	10.45	10.38	52.65	52.69	23.55	23.58
$(EA)_2CuCl_4$	16.10	16.13	4.85	5.38	9.40	9.41	48.00	47.72	23.25	21.36
$(CH_2)_2(NH_3)_2CuCl_4$	8.92	8.97	3.65	3.74	10.45	10.46	53.10	53.08	23.70	23.75

EXPERIMENTAL

The methods of preparation of the compounds were reported by Remy and Laves [3]. The preparations were carried out by dissolving stoichiometric amounts of amine hydrochloride and $CuCl_2 \cdot 2H_2O$ in aqueous or alcoholic solution. Plate-like crystals were obtained which were recrystallized from ethanol. Chemical analysis of the samples were carried out before collecting the data in Table 1. The samples used in this work were fine powder compressed to pellet form with diameter 13 mm and thickness 2 mm. The pressure used for compression was 10 tons cm^{-2}. The d.c. conductivities of the samples were measured under a constant d.c. voltage and by using a potential probe.

The surfaces of each sample were polished and small equal areas on the two surfaces coated with liquid gold and checked to avoid the contact effect. The sample temperature was measured by using a calibrated copper–constantan thermocouple with reference junction at 0°C. The data were collected under constant vacuum to avoid the effect of moisture and were repeated during runs with increasing and decreasing temperature.

RESULTS AND DISCUSSION

Figure 1 shows the relation between ln σ (σ = conductivity) and the reciprocal absolute temperature for the compound $(MeA)_2CuCl_4$ in the

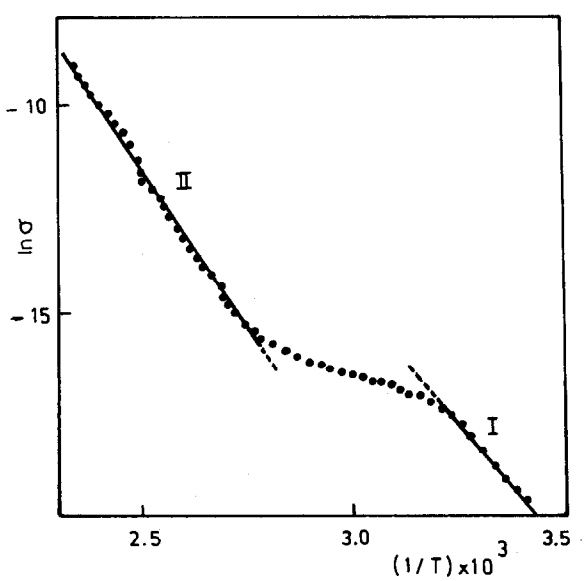

Fig. 1. The relation between ln σ and $1/T$ for the compound $(MeA)_2CuCl_4$.

temperature range which includes the phase transition. From the figure, it is clear that the behaviour obeys the well-known Arrhenius equation

$$\sigma = \sigma_0 \exp(-E/kT) \quad (1)$$

where E is the activation energy, k is the Boltzman constant, T is the absolute temperature and σ_0 is a constant. From the figure, it is clear that two straight lines are obtained with different activation energies $E_I = 1.13$ eV and $E_{II} = 1.39$ eV. The phase transition at $\simeq 313$ K in the electrical conductivity agrees very well with that obtained from the DTA measurements Fig. 2. The colour of the sample is reversibly changed from bright yellow below 313 K to brown above that temperature.

Figure 3 shows the relation between ln σ and $1/T$ for the compound $(EA)_2CuCl_4$. From the figure it is clear that there exists one phase transition at $\simeq 388$ K. This phase is confirmed by the DTA results in Fig. 4. The values of the activation energy as calculated from eqn. (1) are $E_I = 0.58$ eV and $E_{II} \simeq 1.74$ eV corresponding to lines I and II respectively.

Figure 5 shows ln σ versus $1/T$ for the compound $(CH_2)_2(NH_3)_2CuCl_4$ in the range of temperature which includes the phase transition at $\simeq 370$ K. Figure 6 shows the DTA results for the same compound. From the data obtained, it is clear that the DTA thermograph agrees well with the conductivity curve. The values of the activation energy as calculated from Fig. 5 are $E_I = 0.78$ eV and $E_{II} = 0.87$ eV, respectively.

It was found [4–6] that some copper complexes possess thermochromic properties in their solid form, i.e. they show a reversible colour change with temperature. In this respect, there are two basic mechanisms which account for the thermochromic behaviour. On the one hand, experimental evidence

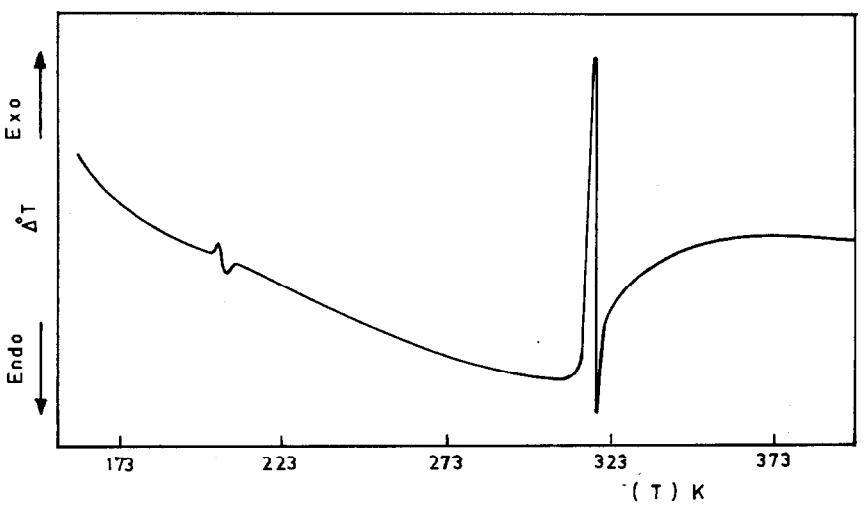

Fig. 2. The relation between $\Delta°T$ and T for the compound $(MeA)_2CuCl_4$.

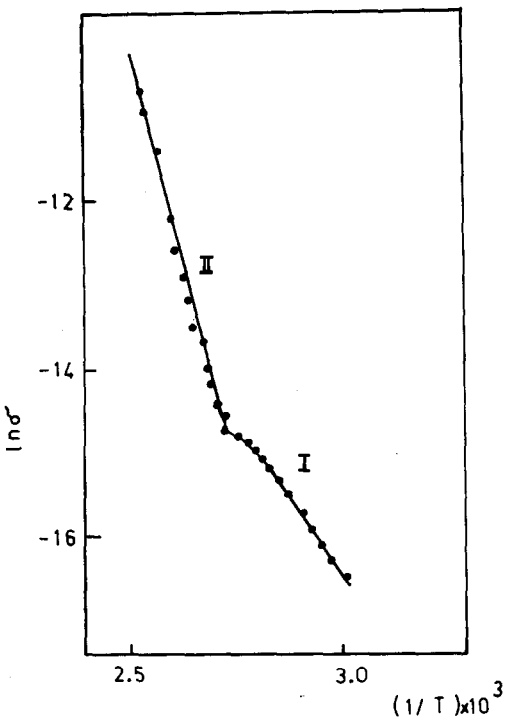

Fig. 3. The relation between ln σ and $1/T$ for the compound $(EA)_2CuCl_4$.

points to the existence of a phase transition in which there is a change in coordination geometry around the copper ion. The mechanism results in a shift in the energy of the electronic transition that lies in the visible region and is accordingly responsible for the thermochromic effect. The driving force of this change is associated with a change in the hydrogen bonding scheme caused by the thermal motion of the organic cation. On the other hand, the thermochromic behaviour may be associated with the temperature dependence of the line width of the electronic absorption band. This is presumably attributed to the presence of a vibrating coupling mechanism. These two mechanisms depend mainly on the compound involved.

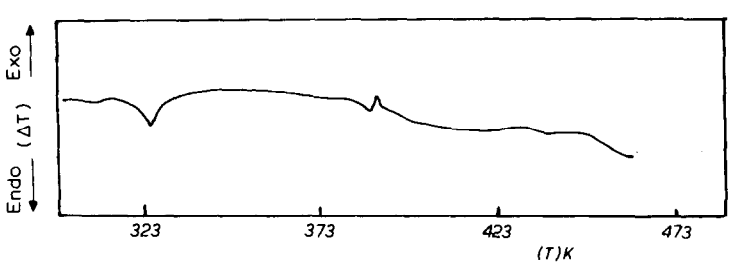

Fig. 4. The relation between ΔT and T for the compound $(EA)_2CuCl_4$.

It may be of interest to make a connection between the change in colour and the values of the activation energy as calculated from the experimental data. Since the colour of the transition metal compounds is produced from

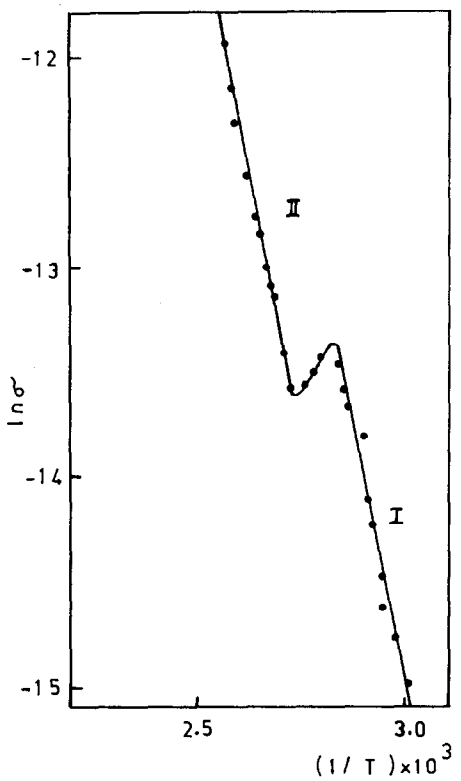

Fig. 5. The relation between ln σ and $1/T$ for the compound $(NH_3)_2(CH_2)_2CuCl_4$.

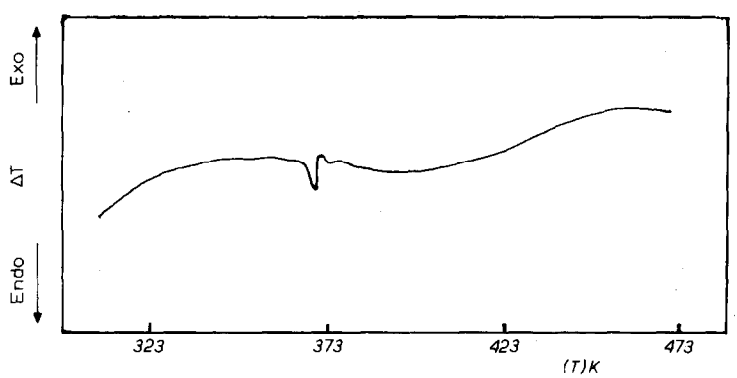

Fig. 6. The relation between ΔT and $1/T$ for the compound $(NH_3)_2(CH_2)_2CuCl_4$.

the vibration of electrons between the incomplete shells [7] and since the energy corresponding to the yellow colour is smaller than that corresponding to the brown colour ($\lambda_{brown} < \lambda_{yellow}$), one can expect that the energy levels in these compounds get broader from each other by increasing temperature passing by the phase transition point, which also agrees with the calculated values of the activation energy.

From the values of the activation energy calculated from eqn. (1), it can be concluded that the compounds have semiconducting properties.

The conductivities and dielectric constants of these samples at low temperatures are now under investigation and will be published later.

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