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THERMAL AND ELECTRICAL STUDIES ON SOME TWO-DIMENSIONAL CHELATED COMPOUNDS

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ABSTRACT

The temperature dependence of the electrical conductivity σ of some two-dimensional chelated compounds ((ODA)$FeCl_4$, $(ODA)_{1/2}$(Cyst)$FeCl_4$, (ODA)$CuCl_4$ and $(ODA)_{1/2}$ (GA)$CuCl_4$, where ODA = octanediammonium ion, Cyst = cystinium ion, GA = glucosammonium ion) was investigated. Differential scanning calorimetry measurements of these compounds show the presence of more than one structural phase transition for each compound. These phase transitions are also observed in the conductivity results. Seebeck voltage measurements show that electrons are the majority charge carriers in all the crystal phases of the complexes.

INTRODUCTION

Of the organometallic complexes, compounds with the general formula $(CH_2)_n(NH_3)_2^+MCl_4$ (where $n = 1, 2, 3$, etc., M is a divalent transition metal and X is a halogen) have evoked great interest in recent years [1–10]. These compounds have a layered perovskite-type crystal structure. The crystal is made up of metal halogen layers of MX_6 octahedra each of which

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shares four corners with neighbouring octahedra in the layer. The metal–halogen distances of the four bridging chlorine atoms are longer than the two terminal halogen distances. The M–X–M bridges are symmetrical.

Previous studies of these two-dimensional compounds have shown that interesting phase transitions occur during heating [5–10]. The importance of studies on the structural phase transitions in these quasi-two-dimensional systems has been shown by studies of low dimensional materials. Such studies will lead to a greater understanding of the physics of magnetism [11], conductivity [12] and other phenomena [13].

From the previous studies on this type of compound several questions need to be answered. What is the correct motion in each phase transition? Does cation diffusion exist? What are the roles of the chain length and the metal in the transitions? What type of charge transfer occurs in these complexes? In order to answer these questions, the successive phase transitions and electrical conduction behaviour of some organoammonium complexes ($(ODA)FeCl_4$, $(ODA)_{1/2}(Cyst)FeCl_4$, $(ODA)CuCl_4$ and $(ODA)_{1/2}(GA)CuCl_4$, where ODA = octanediammonium ion $(C_8H_{22}N_2)^{2+}$, Cyst = cystinium ion $(C_3H_8O_2SN)^+$, GA = glucosammonium ion $(C_6H_{14}O_5N)^+$) were investigated.

EXPERIMENTAL

All the chemicals used were of analytical grade. The iron complexes were prepared by dissolving the appropriate amounts of iron(II) chloride and organoammonium chloride (octanediamine hydrochloride, cystine hydrochloride) in acidified distilled water. Copper complexes were prepared by dissolving the appropriate amounts of copper(II) chloride and organoammonium chloride (octanediamine hydrochloride, glucosamine hydrochloride) in distilled water. The solutions were heated at 80 ° C for about 2 h and were than cooled slowly. The separated crystals were filtered and washed with a little ether. They were kept over P_2O_5 in a purified nitrogen atmosphere. The preparation steps for the iron complexes were performed under nitrogen to prevent the oxidation of Fe^{2+} to Fe^{3+}.

The electrical conductivity measurements were performed on pellets (diameter, 12 mm; thickness, 2 mm) prepared by compression of the powder under a pressure of 1200 kg cm^{-2}. The pellets were coated with silver paste and the resistance was measured using a two-electrode method. All the measurements were carried out under a nitrogen atmosphere and in a thermostat regulated to ± 1.0 ° C. To measure the sign of the carriers which contribute to the electrical conduction of these compounds, a temperature gradient was established across the sample using the axial heat flow method.

IR spectra were obtained using potassium bromide pellets with a Pye Unicam model SP3-100 spectrophotometer.

TABLE 1

Analytical data of the complexes

Complex composition	C (%)	H (%)	N (%)	M (%)	Cl (%)
$(ODA)FeCl_4$	28.01	6.31	8.16	16.27	41.36
	(27.91)	(6.40)	(8.14)	(16.24)	(41.30)
$(ODA)_{1/2}(Cyst)FeCl_4$	21.43	4.76	7.04	14.09	36.03
	(21.38)	(4.84)	(7.13)	(14.22)	(36.15)
$(ODA)CuCl_4$	27.39	6.26	7.97	18.04	40.32
	(27.31)	(6.27)	(7.96)	(18.06)	(40.40)
$(ODA)_{1/2}(GA)CuCl_4$	26.11	5.41	6.07	13.79	30.84
	(26.17)	(5.45)	(6.10)	(13.84)	(30.97)

Calculated data in parentheses; M = chelated ion.

The chemical analysis of the complexes was carried out before data collection (Table 1).

The phase transitions and the enthalpy and entropy changes were detected using a Mettler TA 3000 DSC apparatus.

RESULTS AND DISCUSSION

The IR spectra of the complexes exhibit IR bands characteristic of octahedral MCl_6 groups. The low shift in the characteristic band of the ammonium ions in the amine compounds indicates that they behave as free cations in the complexes. These cations lie between the sandwich layers of the MCl_6 octahedra as previously reported for other similar structures [1–10].

The shift in –OH frequency of the glucosamine in $(ODA)_{1/2}(GA)CuCl_4$ indicates the formation of a hydrogen bond between the OH groups of the glucosamine and the Cl^- ions of octahedral $CuCl_6$.

The characteristic IR bands of the amine hydrochlorides and the complexes are given in Table 2.

The DSC results show small and large peaks for each of the complexes. A summary of the thermodynamic parameters of the transition phases is given in Table 3. For each complex, it can be seen that the main transition precedes the minor transition. It is believed that the main transitions in these systems can be attributed to chain-melting transitions. This can be seen by comparing the enthalpies ΔH of the chain-melting transitions (which can be calculated using Flory's values for the enthalpy of *gauche* bonds [14]) with the observed values. For each complex, the enthalpy of the main transition is higher than the predicted values for chain melting (which is about 6 kcal mol^{-1} for the octanediammonium chain). The observed

TABLE 2

Main IR absorption bands of the compounds in cm^{-1}

Assignment	Compound [a]						
	(1)	(2)	(3)	(4)	(5)	(6)	(7)
$-NH_2$	2900	2970	2960	2950	2890	2900	2850
$-OH$	–	3110	–	–	–	3070	–
$-C{=}O$	–	–	1590	–	1580	–	–
$-FeCl_6$				720	720		
	–	–	–	760	760	–	–
$-CuCl_6$						70	
	–	–	–	–		760	760
						840	840

[a] (1), octanediamine (ODA); (2), glucosamine (GA); (3), cystine (Cyst); (4), $(ODA)FeCl_4$; (5), $(ODA)_{1/2}(Cyst)FeCl_4$; (6), $(ODA)CuCl_4$; (7), $(ODA)_{1/2}(GA)CuCl_4$.

minor transitions can be assigned to dynamic disordering of the chains. The entropy ΔS of a chain oscillating between two equivalent positions has a value of $R \ln 2$ and it has a value of R for free rotation about two axes [9]. However, our results show that the minor transition exceeds that for a simple twofold disorder. This indicates that an additional degree of freedom, probably torsional in nature and/or involving motion of the metal halide framework, is involved. Therefore, we can assume that the organic chains are completely dynamically disordered in the high temperature structure. This final crystal structure is very interesting because of its resemblance to liquid crystals [15].

TABLE 3

Thermodynamic parameters of the phase transitions in the complexes

Complex composition	Transition temperature (K)	Enthalpy ΔH (kcal mol^{-1})	Entropy ΔS (cal mol^{-1} K^{-1})
$(ODA)FeCl_4$	366	10.92	29.83
	455	3.21	7.05
$(ODA)_{1/2}(Cyst)FeCl_4$	316	10.32	32.67
	345	1.62	4.70
	451	3.42	7.58
$(ODA)CuCl_4$	345	9.94	28.81
	475	2.81	5.91
$(ODA)_{1/2}(GA)CuCl_4$	326	9.81	30.09
	358	2.61	7.29
	467	3.74	8.01

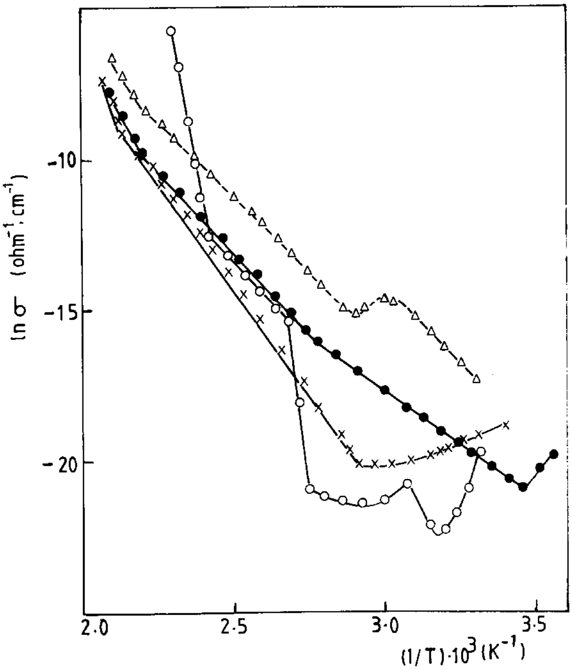

Fig. 1. Effect of temperature on the electrical conductivity of two-dimensional chelated compounds: ●, (ODA)$FeCl_4$; △, $(ODA)_{1/2}$(Cyst)$FeCl_4$; ×, (ODA)$CuCl_4$; ○, $(ODA)_{1/2}$ (GA)$CuCl_4$.

From the results listed in Table 3 the effect of the type of chain on the transition temperature can be observed. In the complexes containing mixed organoammonium ions the transition temperatures lie at lower temperatures than in the complexes containing only octanediammonium ion. This indicates that the strength of the hydrogen bond between the organoammonium ion and the Cl^- ions is weaker in the complexes containing mixed chains.

In order to determine the electrical conduction and the type of charge carriers in the various phases of the complexes, d.c. electrical conductivity σ and Seebeck coefficient measurements θ were performed at various temperatures.

The conductivity results show that all the investigated complexes behave as ohmic semiconductors at room temperature. For an applied potential of up to 100 V (ca. 500 V cm^{-1}), plots of log I vs. log V show a linear behaviour with slopes within the range 1.0–1.1. For $(ODA)_{1/2}$(Cys)$FeCl_4$ the linearity is observed at lower voltage (ca. 300 V cm^{-1}).

The relationship between ln σ of the complexes and $1/T$ is shown in Fig. 1. All the plots in this figure show an approximately similar trend. Each plot consists of many straight lines with different slopes corresponding to different activation energies. The temperatures at which the breaks occur in Fig. 1 are of the same order as the temperatures of the phase transitions observed

TABLE 4

Electrical conductivity data of the complexes

Complex composition	300 K	300–330 K		360–390 K		410–435 K	
	σ_1 (ohm^{-1} cm^{-1})	σ_2 (ohm^{-1} cm^{-1})	E_2 (eV)	σ_3 (ohm^{-1} cm^{-1})	E_3 (eV)	σ_4 (ohm^{-1} cm^{-1})	E_4 (eV)
$(ODA)FeCl_4$	2.78×10^{-9}	6.10×10^{-9}	0.62	4.56×10^{-7}	0.62	2.58×10^{-6}	0.77
$(ODA)_{1/2}(Cyst)FeCl_4$	2.77×10^{-8}	8.33×10^{-8}	0.94	1.67×10^{-6}	0.90	3.04×10^{-5}	–
$(ODA)CuCl_4$	5.61×10^{-9}	3.40×10^{-9}	–	4.14×10^{-8}	1.23	2.26×10^{-6}	–
$(ODA)_{1/2}(GA)CuCl_4$	2.78×10^{-9}	2.79×10^{-10}	–	1.24×10^{-7}	0.86	8.30×10^{-6}	4.6

E = activation energy; σ_2 = specific conductivity at 310 K; σ_3 = specific conductivity at 370 K; σ_4 = specific conductivity at 410 K.

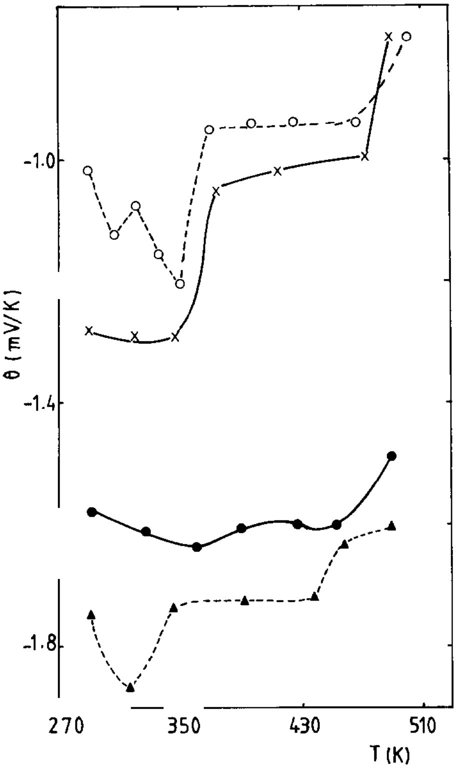

Fig. 2. Effect of temperature on the Seebeck coefficient of two-dimensional complexes: ●, (ODA)$FeCl_4$; ▲, $(ODA)_{1/2}$(Cyst.)$FeCl_4$; ×, (ODA)$CuCl_4$; o, $(ODA)_{1/2}$(GA)$CuCl_4$.

using DSC measurements (Table 3). The activation energies E_a for each sample can be calculated using the Arrhenius equation [16] in the temperature range where the plots ln σ vs. $1/T$ are linear. The conductivity data are given in Table 4. It can be seen that a wide range of conductivity values are observed lying in the region of a semiconductor.

The electrical measurements on all the compounds show that there is no electrical polarization at the electrodes, i.e. after releasing the potential there is no appreciable reversible electromotive force and at very low potential (0.25 V) the current is kept constant. These observations suggest that the conduction is mainly electronic.

Plots of Seebeck voltage θ as a function of temperature are shown in Fig. 2. It can be seen that changes in θ values occur at the phase transition temperatures. All θ values are negative, which indicates that electrons are the major charge carriers in all phases of the complexes. In addition, it can be seen from Fig. 2 that the concentrations of charge carriers in the higher temperature phases are lower than those found in the lower temperature phases. This means that the concentration of charge carriers decreases with increasing disorder of the crystal structure. However, the conductivity results

(Fig. 1) show an increase in σ value with increasing temperature. This implies that the mobility of the charge carrier increases with increasing temperature, i.e. with increasing disorder of the crystals.

To estimate the mobility of the charge carriers in the complexes the equation $\sigma = eN_0\mu$ [16] was used with a charge carrier concentration $N_0 = 10^{21}$. The value of mobility μ is in the range 10^{-7}–10^{-10} cm^2 V^{-1} s^{-1}. The fact that the value of μ is much smaller than 1 cm^2 V^{-1} s^{-1} [17] means that the band model cannot be used to describe the mechanism of conductance in the complexes. The hopping model has been used previously to describe the mechanism of conductance for μ values smaller than 1 cm^2 V^{-1} s^{-1} which increase with temperature [18]. This seems to be the case in the present system. However, further investigation of these two-dimensional crystal structures, including the effect of γ radiation on chelated compounds having the same transition metal and different ligands, may provide us with more information on the mechanism of the charge transfer. These studies will be published later.

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