

**γ -IRRADIATION EFFECTS ON THE ELECTRICAL CONDUCTIVITY
OF SOME TWO-DIMENSIONAL COMPLEXES: RMnCl_4 , RCoCl_4
AND $\text{RMn}_{0.5}\text{Co}_{0.5}\text{Cl}_4$ ($\text{R} = \text{H}_3\overset{+}{\text{N}}-(\text{CH}_2)_8-\overset{+}{\text{N}}\text{H}_3$)**

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ABSTRACT

DTA, d.c. conductivity and thermoelectric power of the compounds RMnCl_4 , RCoCl_4 and $\text{RMn}_{0.5}\text{Co}_{0.5}\text{Cl}_4$ ($\text{R} = \text{H}_3\overset{+}{\text{N}}-(\text{CH}_2)_8-\overset{+}{\text{N}}\text{H}_3$) were measured over a temperature range of 300–500 K. Both the DTA and the d.c.-conductivity results show the presence of many phase transitions in each of the complexes investigated. The conductivity results are explained on the basis of an electron-hopping mechanism. The effect of γ -irradiation on the conductivity data and the type of crystal phase are investigated and discussed.

INTRODUCTION

In recent years there has been great interest in studying the electrical properties of the inorganic transition-metal complexes, due to the observation of the variation in their electrical conductivity with a change in valency

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of the transition-metal ion [1] and their chemical and crystal structures. The electrical properties of these compounds are sensitive to many variables [2] such as irradiation with energetic γ radiation [3–5], which has a major effect on the concentration and mobility of charge carriers in chelated compounds.

The purpose of this work was to study the effect of γ radiation on the electrical properties of some two-dimensional compounds: RMnCl_4 , RCoCl_4 and $\text{RMn}_{0.5}\text{Co}_{0.5}\text{Cl}_4$, where $\text{R} = \text{H}_3\text{N}^+(\text{CH}_2)_8\text{NH}_3^+$. These compounds form part of a series of two-dimensional chelated compounds [6] whose structure consists of puckered layers of metal ion(II) octahedrally separated by the protonated diammonium ion. Previous investigations on similar layered compounds have shown that they exhibit interesting phase transitions during thermal heating [7–11]. Therefore, the present studies will provide information on the type of charge carrier and on the mechanism of its migration in these two-dimensional compounds as well as give us some idea about the type of phase transitions occurring on heating these irradiated and unirradiated complexes.

EXPERIMENTAL

The metal chelates $\text{H}_3\text{N}-(\text{CH}_2)_8-\text{NH}_3\text{MnCl}_4$ and $\text{H}_3\text{N}-(\text{CH}_2)_8-\text{NH}_3\text{CoCl}_4$ were prepared from pure reagents according to the procedure described previously [12]. Mixed crystals, $\text{H}_3\text{N}-(\text{CH}_2)_8-\text{NH}_3\text{Mn}_{0.5}\text{Co}_{0.5}\text{Cl}_4$, were prepared by adding absolute ethanol to a hot saturated solution of the pure components.

The electrical conductivities (σ) of γ -irradiated and unirradiated compounds were measured under vacuum over a temperature range of 300–500 K. The measurements were performed on pellets (diameter 7 mm and thickness 3 mm), using the method reported previously [13]. The Seebeck coefficient measurements were made at temperature intervals of $\Delta T \approx 40$ K (against platinum).

Infrared (IR) spectra of the compounds investigated were recorded on KBr pellets using a Pye Unicam Model SP3-100 spectrophotometer.

The phase-transition points, enthalpies and the entropy changes were detected by DTA and DSC apparatus (model Mettler TA 3000).

The complexes investigated were irradiated with γ rays using a ^{60}Co - γ cell with a dose rate of 3.6×10^3 rad h^{-1} for 333 h.

Elemental analysis was done before collecting the data and confirmed the above chemical structure.

RESULTS AND DISCUSSION

The IR spectra of the complexes investigated showed the characteristic absorption bands expected in these compounds. IR spectra obtained for the

TABLE 1

The thermodynamic data for the phase transitions in the complexes investigated: the values for γ -irradiated (1.2 Mrad) samples are given in parentheses

Complex composition	Transition temperature (K)	Enthalpy ΔH (kcal mol ⁻¹)	Entropy, ΔS (cal mol ⁻¹ K ⁻¹)
H ₃ N-(CH ₂) ₈ -NH ₃ MnCl ₄	332 (317)	1.0 (0.9)	3.01 (2.83)
	355 (353)	1.2 (1.1)	3.38 (3.11)
	390 (390)	8.6 (8.6)	22.05 (22.05)
H ₃ N-(CH ₂) ₈ -NH ₃ Mn _{0.5} Co _{0.5} Cl ₄	317 (307)	1.2 (1.0)	3.78 (3.25)
	344 (340)	0.8 (0.8)	2.32 (2.35)
	390 (390)	1.5 (1.5)	3.85 (3.85)
	408 (408)	8.1 (8.1)	19.85 (19.85)
H ₃ N-(CH ₂) ₈ -NH ₃ CoCl ₄	330 (320)	1.4 (1.1)	4.24 (3.43)
	344 (335)	1.7 (1.6)	4.94 (4.77)
	408 (406)	1.8 (1.7)	4.41 (4.19)
	430 (430)	8.4 (8.4)	19.53 (19.53)

irradiated complexes showed no significant changes in the number and positions of the IR bands in comparison with the unirradiated samples.

Table 1 shows the transition temperatures and the thermodynamic-function values for all the irradiated and unirradiated compounds studied. In all cases, the minor transitions precede the main transitions. The irradiation causes a shift in the position of the first phase transition in each complex investigated. This shift is not observed in the higher temperature phase transitions. Therefore, it may be expected that at higher temperatures a common mechanism is responsible for the phase transitions in irradiated and unirradiated compounds. The main higher temperature phase transition may be attributed to a chain-melting transition. This can be seen by comparing the higher enthalpy values obtained in the main phase transition with those calculated for the chain-melting transition (about 6 kcal mol⁻¹) by using Flory's values for the enthalpy of *gauche* bonds [14]. On the other hand, the entropy values obtained for the minor transitions indicate that these transitions can be assigned to the dynamic disordering of the organic chains [15-17]. This disorder was affected by γ irradiation (Table 1).

The electrical conductivities (σ) of complexes investigated were measured over the temperature range 300-500 K. The results are summarized in Table 2 and given in Fig. 1. It can be seen that the measured conductivity values lie in the semiconductor range and, remarkably, change with chemical composition. The conductivity (Fig. 1) shows many phase transitions, each corresponding to an abrupt change of σ and leading to a new structural modification in the complexes. The temperatures at which the abrupt change in σ -values occurs agree well with those obtained by DTA measurements (Table 1).

TABLE 2

The electrical conductivity data of the irradiated (σ^*) and unirradiated (σ) samples under investigation

Complex composition	Temperature range (K)	$\sigma(T)$ ($\text{Ohm}^{-1} \text{cm}^{-1}$)	E_a (eV)	Phase-transition temperature ^a (K)
$\text{H}_3\text{N}-(\text{CH}_2)_8-\text{NH}_3\text{MnCl}_4$	300-320	$\sigma(310) = 5.04 \times 10^{-7}$ $\sigma^*(310) = 1.01 \times 10^{-5}$		331, 353, 385. 320, 350, 390
	390-500	$\sigma(450) = 5.03 \times 10^{-6}$ $\sigma^*(450) = 5.05 \times 10^{-6}$	1.18 1.18	
$\text{H}_3\text{N}-(\text{CH}_2)_8-\text{NH}_3\text{Mn}_{0.5}\text{Co}_{0.5}\text{Cl}_4$	300-320	$\sigma(310) = 4.63 \times 10^{-10}$ $\sigma^*(310) = 5.61 \times 10^{-9}$		317, 392, 413. 312, 392, 413
	320-390	$\sigma(385) = 2.51 \times 10^{-7}$ $\sigma^*(385) = 3.55 \times 10^{-7}$	0.98 0.60	
	410-500	$\sigma(450) = 4.53 \times 10^{-5}$ $\sigma^*(450) = 4.50 \times 10^{-5}$	1.74 1.74	
$\text{H}_3\text{N}-(\text{CH}_2)_8-\text{NH}_3\text{CoCl}_4$	300-320	$\sigma(310) = 4.53 \times 10^{-5}$ $\sigma^*(310) = 1.36 \times 10^{-4}$		328, 345, 408, 418, 432.
	365-408	$\sigma(385) = 9.19 \times 10^{-7}$ $\sigma^*(385) = 9.22 \times 10^{-7}$	0.85 0.83	321, 350, 408 418, 432
	408-418	$\sigma(410) = 1.67 \times 10^{-5}$ $\sigma^*(410) = 1.71 \times 10^{-5}$	5.7 5.7	
	435-500	$\sigma(450) = 1.22 \times 10^{-2}$ $\sigma^*(450) = 1.22 \times 10^{-2}$	1.33 1.33	

^a The temperature at which the break in the conductivity values occurred.

Figure 1 shows that at higher temperatures the conductivities, σ , could be well represented by different straight lines verifying the Arrhenius equation $\sigma = \sigma_0 \exp(-E_a/kT)$. The activation energies, E_a , for each phase of the complexes investigated were calculated using the least-squares method and are given with the temperatures at which the breaks in σ appear and the other conductivity data in Table 2. The higher activation energy values obtained at higher temperatures are attributed to the intrinsic dissociation occurring in the complexes due to the chain melting of alkylene diammonium, as mentioned above. In this higher temperature range the conductivity was found to increase in the order $\text{RCoCl}_4 > \text{RMn}_{0.5}\text{Co}_{0.5}\text{Cl}_4 > \text{RMnCl}_4$.

The conductivity results given in Fig. 1 show that the conductivity at lower temperatures, before the first phase transition, is almost temperature independent. This behaviour has been observed in some inorganic metals such as Si-Au [18] and was interpreted on the basis of a hopping model [19] which describes the behaviour of a disordered system with an electron just below the Fermi level hopping to a distant state for which the energy required is infinitely small.

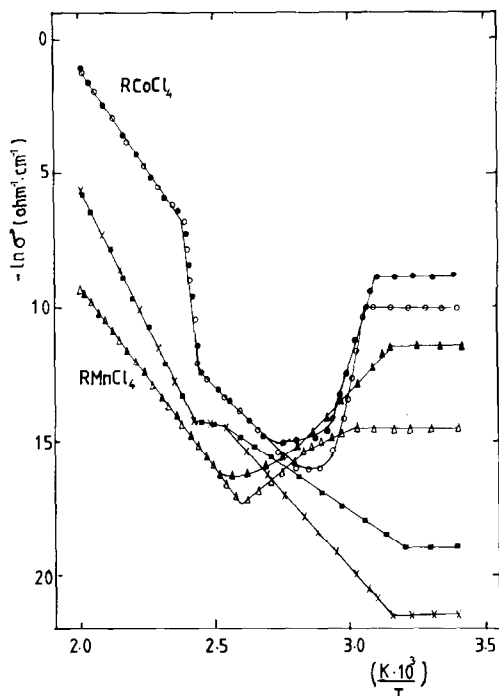


Fig. 1. The effect of temperature on the electrical conductivity values of the γ -irradiated (1.2 Mrad) and unirradiated complexes: \times , unirradiated RMnCl_4 ; \blacksquare , irradiated RMnCl_4 ; \circ , unirradiated RCoCl_4 ; \bullet , irradiated RCoCl_4 ; \triangle , unirradiated $\text{RMn}_{0.5}\text{Co}_{0.5}\text{Cl}_4$; \blacktriangle , irradiated $\text{RMn}_{0.5}\text{Co}_{0.5}\text{Cl}_4$.

The effect of γ irradiation on the electrical conductivities of the complexes investigated was studied using a radiation dose of 1.2 Mrad. Plots of $\ln \sigma$ versus $1/T$ for the irradiated complexes show the same behaviour as those obtained for the unirradiated ones (Fig. 1). The conductivity data of the irradiated complexes are summarized and listed with those of the unirradiated compounds in Table 2, from which it can be seen that, at lower temperatures, below the first phase transition, the σ values of the irradiated complexes are higher than those of the corresponding unirradiated ones. This behaviour can be explained on the basis of an increase in the electron concentration by the interaction of γ rays with divalent metal ions ($\text{M}^{2+} = \text{Co}^{2+}$ or Mn^{2+})

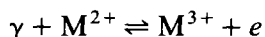


Figure 1 shows that, in the higher temperature range, the conductivities of the irradiated complexes coincide well with those of the unirradiated ones. At this higher temperature range, the disorder occurring in the crystal is very high and the concentration of charge carriers induced by γ rays is very small compared with that due to the intrinsic disorder occurring in the crystal lattice, as is shown by Seebeck voltage measurements.

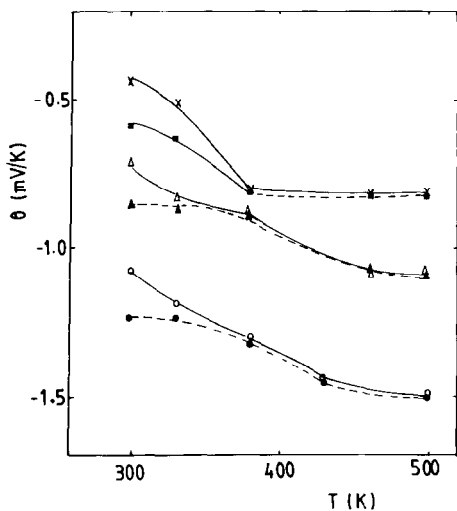


Fig. 2. Dependence of the Seebeck coefficient on temperature for the γ -irradiated (1.2 Mrad) and unirradiated complexes: \times , unirradiated RMnCl_4 ; \blacksquare , irradiated RMnCl_4 ; \circ , unirradiated RCoCl_4 ; \bullet , irradiated RCoCl_4 ; Δ , unirradiated $\text{RMn}_{0.5}\text{Co}_{0.5}\text{Cl}_4$; \blacktriangle , irradiated $\text{RMn}_{0.5}\text{Co}_{0.5}\text{Cl}_4$.

The Seebeck voltage measurements were carried out on the irradiated and unirradiated complexes at temperatures before and after each anomaly. The results are presented in Fig. 2 from which it can be seen that, in all phases of the irradiated and unirradiated complexes, the Seebeck voltage is negative and the number of charge carriers increases in the lower temperature phases on irradiation. On the other hand, in the higher temperature phases, the measured Seebeck coefficients, θ , are almost equal. This indicates that the number of charge carriers in these higher temperature phases is not affected by radiation. At the same time the Seebeck voltage results show that the increase in the number of charge carriers in the higher temperature phases compared to that in the lower temperature ones is too small to be responsible for the larger change in the electrical conductivity between these different phases (Fig. 1). The large increase in σ in the higher temperature phases is attributed mainly to the change in the mobility of the charge carriers in the different phases.

CONCLUSION

The DTA and d.c. conductivity of the complexes investigated showed many phase transitions during heating. The number of phases was not changed by irradiation. Both conductivity and thermoelectric power measurements indicate that a hopping transport of electrons through the different crystal lattices is the predominant conduction process for the whole

range of temperatures investigated. γ -Irradiation led to increased conductivity values for the lower temperature phases. This increase in σ on irradiation was explained on the basis of the increase in the concentration of electrons on irradiation.

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