

## Photoconductivity and dielectric constant studies of some organic complexes

M.M. El-Desoky <sup>a</sup>, M.A. Ahmed <sup>b</sup> and H.H. Higazy <sup>c</sup>

<sup>a</sup> *Physics Department, Faculty of Science, Al-Azhar University, Cairo (Egypt)*

<sup>b</sup> *Physics Department, Faculty of Science, Cairo University, Giza (Egypt)*

<sup>c</sup> *Spectroscopy Department, National Research Centre, Dokki, Cairo (Egypt)*

(Received 14 December 1990)

### Abstract

The photocurrent of the two-dimensional system for  $(\text{CH}_2)_2(\text{NH}_3)_2\text{MCl}_4$  ( $\text{M} = \text{Co}^{2+}$  and  $\text{Cu}^{2+}$ ) as a function of temperature, exposure time and returning time has been measured. The activation energy and photoconductivity values were calculated. Saturation of the photoconducting current was reached after exposure for about 25 min. The photocurrents showed a decrease in value with increasing temperature. The dielectric constant was measured, also as a function of temperature and frequency and the electric dipole moment was calculated at different temperatures.

### INTRODUCTION

In the past few years, many authors [1–4] have studied the photoconductivity of organic compounds. The photocurrent produced in such compounds is always dependent on the intensity of the exciting light, the temperature, the applied electric or magnetic field, the surface conditions and the ambient atmosphere. In many of the organic compounds that have semiconducting properties, the time required for the photoconductivity (photocurrent) to change as a function of exciting light intensity is determined by the life-time of the charge carriers [5].

The crystal structure of some organic complexes containing,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  have been determined previously [6,7]. The compounds under investigation here, of general formula  $(\text{CH}_2)_2(\text{NH}_3)_2\text{MCl}_4$  ( $\text{M} = \text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ), are isomorphous with those determined by Willett and Riedel [6]. These are both complexes of the simplest two-dimensional system, consisting of  $\text{MCl}_4^{2-}$  anions with alkylene diammonium groups sandwiched between the layers to form a layered perovskite-type structure. The  $\text{NH}_3$  groups are expected to be hydrogen-bonded to the  $\text{M}-\text{Cl}$  network, which results in the monoclinic unit cell.

On first measurement of the electric conductivity (dark conductivity), a relatively large polarisation in the sample was obtained, even at room

temperature; therefore the dielectric constant measurements have to be considered.

The basis of the present work depends on the increase of the dielectric constant with temperature near the transition points of the compounds, as well as the change in their photoconductivity with exposure time.

## EXPERIMENTAL

Analar grade  $\text{CoCl}_2$ ,  $\text{CuCl}_2$  and  $(\text{CH}_2)_2(\text{NH}_3)_2\text{Cl}_2$  were used as starting materials in the preparation of the two compounds under investigation. As previously reported [8], the starting materials were mixed initially in stoichiometric ratio in ethanol solution. The mixture was heated under a pure nitrogen atmosphere for about 1 h. The precipitate was filtered, dried and recrystallised from ethanol. For dielectric constant measurements, the samples were prepared in fine powdered form, pressed into pellets of diameter 14 mm and thickness 1 mm under pressure of  $2 \times 10^5 \text{ lb in}^{-2}$ . The two surfaces of each sampled were coated with gold paste (BDH, England). The dielectric constant data were collected using the circuit reported in ref. 9. Photoconductivity measurements were also carried out using the bulk technique [10] with a 450 W Osram xenon arc lamp as an excitation source. A liquid filter was used to prevent the heat from affecting the dispersion of the PMQII quartz prism monochromator used for selecting the exciting wavelength. The photoconducting current was measured using the potential probe method with an applied d.c. voltage [11].

## RESULTS AND DISCUSSION

Figure 1 shows the dependence of the photocurrent on the exposure time at different temperatures for  $(\text{CH}_2)_2(\text{NH}_3)_2\text{CoCl}_4$ . A gradual increase in the photoconducting current was obtained with time. After about 25 min,

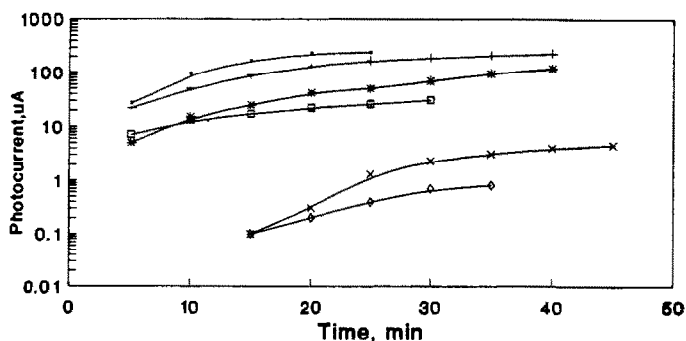


Fig. 1. Relation between photocurrent and time at constant temperature for the  $(\text{CH}_2)_2(\text{NH}_3)_2\text{CoCl}_4$  complex: •, 268 K; +, 273 K; \*, 280 K; □, 283 K; ×, 288 K; ◇, 293 K.

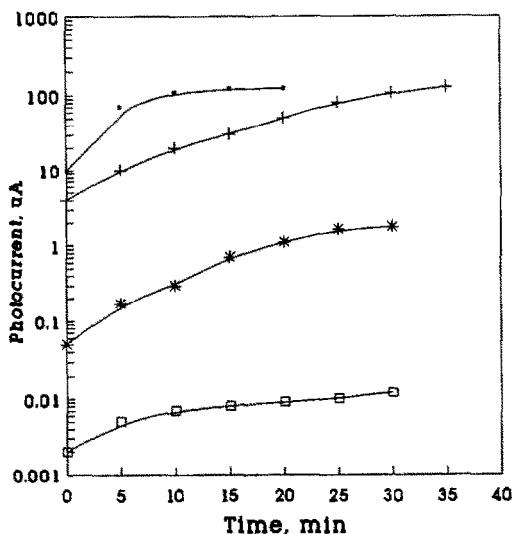


Fig. 2. Relation between photocurrent and time at constant temperature for the  $(\text{CH}_2)_2(\text{NH}_3)_2\text{CuCl}_4$  complex: •, 268 K; +, 273 K; \*, 278 K; □, 283 K.

saturation was reached. This means that no further charge carriers can be generated. In other words, one may expect that the rate of generation of the photocarrier is equal to the rate of recombination.

The same behaviour was observed for  $(\text{CH}_2)_2(\text{NH}_3)_2\text{CuCl}_4$  (see Fig. 2). Comparing Figs. 1 and 2, it can be seen that the values of the photocurrent for the  $\text{Co}^{2+}$  complex are much higher than those of the  $\text{Cu}^{2+}$  complex, under almost the same conditions. This means that more energy (light energy) is required to activate the photocurrent in the case of the  $\text{Cu}^{2+}$  complex. It seems likely that the electronic distribution of  $\text{Cu}^{2+}$  contributes to this behaviour. Table 1 shows the calculated activation energy values which confirm our predictions concerning the semiconducting properties of the compounds (see Fig. 1). Figure 3 plots the photocurrent against the absolute temperature for the two compounds with  $M = \text{Co}^{2+}$  and  $\text{Cu}^{2+}$ . The data are collected at constant exposure time. From the figure, it is clear that, for both compounds, the value of the photocurrent increases with decreasing temperature. This may be due to localisation of the charge carriers at low temperature which decreases the probability of electron-phonon scattering.

TABLE 1

Photoconductivity and activation energy values for  $(\text{CH}_2)_2(\text{NH}_3)_2\text{MCl}_4$  ( $M = \text{Co}^{2+}, \text{Cu}^{2+}$ )

Compound	$\sigma$ ( $\text{M}^{-1} \text{cm}^{-1}$ ) at 286 K	$E$ (eV)
$(\text{CH}_2)_2(\text{NH}_3)_2\text{CoCl}_4$	$8.3 \times 10^{-6}$	0.35
$(\text{CH}_2)_2(\text{NH}_3)_2\text{CuCl}_4$	$1.4 \times 10^{-11}$	0.52

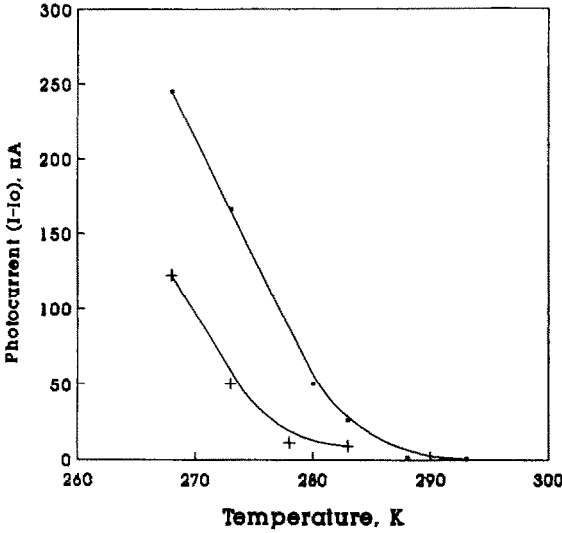


Fig. 3. Relation between photocurrent and temperature for the  $(\text{CH}_2)_2(\text{NH}_3)_2\text{MCl}_4$  ( $\text{M} = \text{Co}, \text{Cu}$ ) complex at constant exposure time:  $\cdot$ ,  $\text{CoCl}_4$ ;  $+$ ,  $\text{CuCl}_4 (\times 10^{-2})$ .

Such behaviour is the inverse of the dark conductivity of the two-dimensional complexes [12]. As the temperature of the sample is increased, the thermal energy produced becomes sufficient to increase the electron-phonon scattering and, at the same time, decrease the photoconducting current. In other words, if the time required for the photocurrent to reach saturation (Fig. 1) and the decay time required for the trapped carriers to be thermally released (Fig. 3) are much greater than the lifetime of the carriers, one may expect the capture of the photogenerated free carriers [5]. This agrees well with our predictions at high temperature. This valuable information on the inverse behaviour of the samples under investigation suggests that further studies concerning their industrial applications at low temperatures may be worthwhile.

Figure 4 shows the relation between the returning time and the absolute temperature at constant exposure time. Although the photocurrent at 268 K is increasing (Fig. 3) the returning time at 273 K is greater than that at 268 K. So, from this result, the most suitable temperature, at which a maximum returning time was obtained, is 273 K. This point enhances the above suggestion concerning the application of these samples in the manufacture of photosensors, especially for low temperature uses.

The dielectric constant measurements for the two compounds were made as a function of temperature and frequency; typical curves were obtained. See, as an example, Fig. 5 which shows the behaviour of the  $\text{Co}^{2+}$  complex. To a large extent, the shape of the curves for the dielectric constants are similar to those of the two-dimensional systems [9]. This leads to the well-known behaviour of the dielectric constant of such complexes, which is

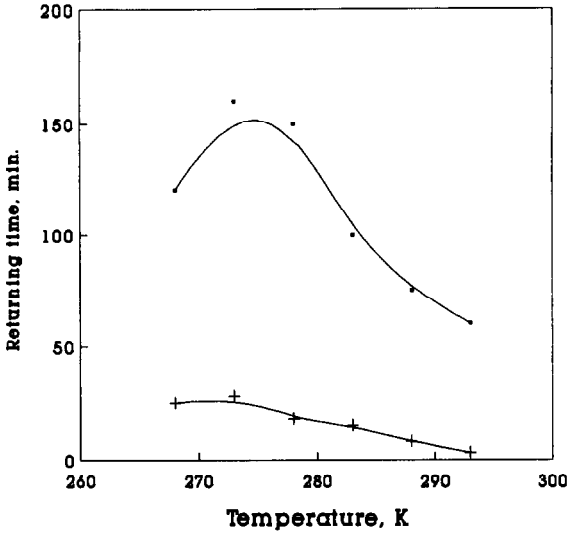


Fig. 4. Relation between returning time and temperature for the  $(\text{CH}_2)_2(\text{NH}_3)_2\text{MCl}_4$  ( $\text{M} = \text{Co}, \text{Cu}$ ) complex: \*,  $\text{CoCl}_4$ ; +,  $\text{CuCl}_4$ .

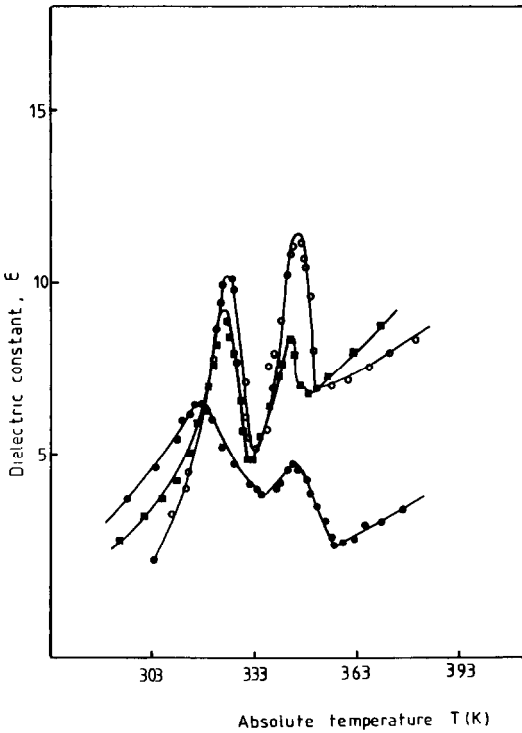


Fig. 5. Relation between the dielectric constant and temperature of the compound  $(\text{CH}_2)_2(\text{NH}_3)_2\text{CoCl}_4$  at different frequencies: ○, 1 kHz; ■, 10 kHz; ●, 100 kHz.

TABLE 2

Electric dipole moments for  $(\text{CH}_2)_2(\text{NH}_3)_2\text{MCl}_4$  ( $\text{M} = \text{Co}^{2+}, \text{Cu}^{2+}$ )

$(\text{CH}_2)_2(\text{NH}_3)_2\text{CoCl}_4$			$(\text{CH}_2)_2(\text{NH}_3)_2\text{CuCl}_4$		
$T$ (K)	$\mu$ (C cm $\times 10^{-20}$ )	$f$ (kHz)	$T$ (K)	$\mu$ (C cm $\times 10^{-20}$ )	$f$ (kHz)
323	24.9	1	325	75.00	1
344	25.5	1	347	41.40	1
313	30.1	10	326	71.20	10
353	24.4	10	355	67.90	10
329	25.4	100	316	59.56	100
342	25.9	100	345	53.10	100

characterised by the presence of more than one phase transition and the appearance of a gradual change in the crystal structure. Figure 5 shows that the dielectric constant tends to increase with increasing temperature until it reaches maximum at about 323 K. This maximum value is shifted slightly to lower temperatures by increasing the applied frequencies. Increasing the temperature continuously leads to another peak at about 348 K. The electric dipole moments at the peak values are calculated from the equation [13]

$$\chi = \frac{\kappa}{N\mu^2} \left[ T - \frac{N\mu^2\beta}{\kappa} \right]$$

where  $\chi = (\epsilon - 1)\epsilon_0$ , and are listed in Table 2. Comparing the data of the dielectric constant and electric dipole moment, it is clear that the expected gradual change in the electronic configuration of the compounds with temperature is responsible for the increase in the dielectric constant before the phase transition points. This may be due to the presence of the organic group between the layers.

In conclusion, one can say that the two-dimensional system as represented in the investigated compounds follows the well-known behaviour of the dielectric constant. At the same time, the photoconducting current of the two-dimensional system behaves inversely with the dark current conduction.

## REFERENCES

- 1 B. Rosenberg, *J. Chem. Phys.*, 31 (1959) 238; 34 (1961) 63.
- 2 M. Wilk, *Z. Electrochem.*, 64 (1960) 930.
- 3 M. Kleinerman and S.P. McGlynn, *J. Chem. Phys.*, 37 (1962) 1339.
- 4 L.N. Ionov and I.A. Akimov, *Soviet Phys. Semicond.*, 5 (1972) 1756.
- 5 K.C. Kao and W. Hwang, *Electrical Transport in Solids*, Elsevier, New York, 1981, Chapter 6.
- 6 R.D. Willett and E.F. Riedel, *Chem. Phys.*, 8 (1975) 112.
- 7 W.E. Hatfield and T.T. Hodgson, *Inorg. Chem.*, 26 (1978) 59.
- 8 M.A. Ahmed, M.M. El-Desoky and F.A. Radwan, *Aust. J. Phys.*, 41 (1988) 85.
- 9 M.A. Ahmed, M.M. El-Desoky and F.A. Radwan, *Thermochim. Acta*, 105 (1986) 295.

- 10 H. Inoue, T. Takiuchi and E. Imoto, *Kogyo Kagaku Zasshi*, 65 (1962) 1291.
- 11 M.A. Ahmed and F.A. Radwan, *J. Phys. Chem. Solids*, 49 (1988) 1385.
- 12 M.A. Ahmed, H.A. Mousa and F.A. Radwan, *Mat. Sci.*, 23 (1989) 4345.
- 13 T. Mitsui, I. Tasuzaki and A. Nakamura, *An Introduction to the Physics of Ferroelectrics*, Gordon and Breach, New York, 1976, p. 198.