

Temperature effect on magnetic and electrical properties of the compound $\text{Fe}(\text{DMSO})_2\text{Cl}_2$

M. A. AHMED

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

M. A. MOUSA

Chemistry Department, Faculty of Science, Benha University, Benha, Egypt

Sulphoxide ligands have two potential donor sites. The lighter or more highly charged metal ions favour oxygen coordination while a few heavier metals prefer the sulphur donor sites [1, 2]. However, some sulphoxide complexes were found to contain both S- and O-bonded sulphoxide ligands [3, 4].

X-ray structural analysis on $(\text{FeCl}(\text{DMSO})_5)(\text{Fe}_2\text{Cl}_6\text{O})$ complex showed [5] that the position of the dimethylsulphoxide molecule (DMSO) became distorted between two positions with increasing temperature. The disorder in this compound is due to the tendency of the angle of the oxobridge of the anion ($\text{Cl}_3\text{Fe}-\text{O}-\text{FeCl}_3$) to straighten out, the effect being transmitted to the cation via the short Cl-S contact.

In this letter we report a study of the effect of temperature on the magnetic susceptibility, dielectric constant and electrical conductivity of the neutral complex $(\text{DMSO})_2\text{FeCl}_2$. This complex was found to have a distorted square planar complex at room temperature, with two chloride ions and two oxygens of sulphoxide groups lying around the Fe^{2+} ions [5]. Such studies may yield information about the effect of temperature on the structure and the donor sites of DMSO in this type of complex.

The $(\text{Fe}(\text{DMSO})_2\text{Cl}_2)$ complex was prepared by slow evaporation of acidified alcoholic solutions of the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and DMSO in molar ratio 1:2, respectively. A stream of purified nitrogen gas was allowed to pass through the solution to prevent the oxidation of the ferrous ions. After concentration of the solution by evaporation, the complex was separated as yellow crystals. It was recrystallized from hot acetone. Complete drying of the sample (over P_2O_5) and its grinding was carried out in a glove box filled with oxygen-free nitrogen gas. The analytical data showed that the prepared complex had a chemical composition of $(\text{Fe}(\text{DMSO})\text{Cl}_2)$.

The sample was prepared for measurements in a pellet form of diameter 16 mm and thickness 1 mm. The pressure used for compression was fixed at 15 ton cm^{-2} in both dielectric constant and electrical conductivity. The two surfaces of the sample were polished and small equal areas on them were covered with liquid gold and checked to avoid contact effects. The sample temperature was measured using a calibrated copper-constantan thermocouple with reference junction at 0°C .

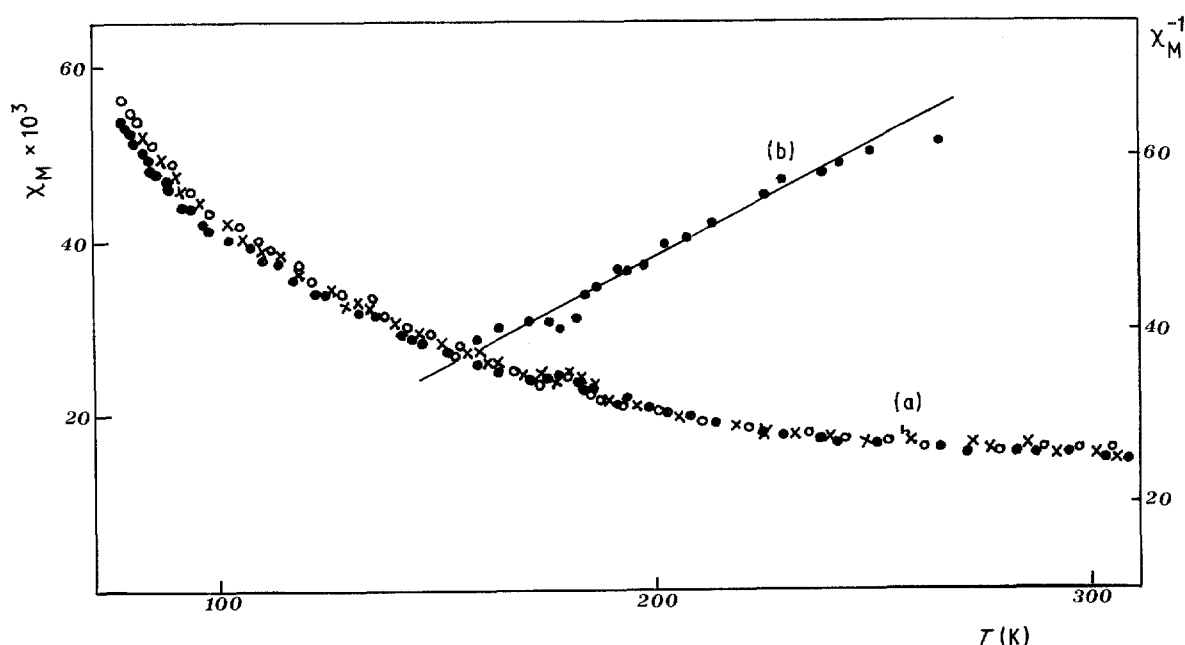


Figure 1 (a) The relation between the corrected molar magnetic susceptibility and absolute temperature at different cooling fields in $(\text{CH}_3)_2\text{SO}_2\text{FeCl}_2$: (●) zero magnetic field; (x) 1820 Oe; (○) 3600 Oe. (b) The relation between the reciprocal magnetic susceptibility and absolute temperature.

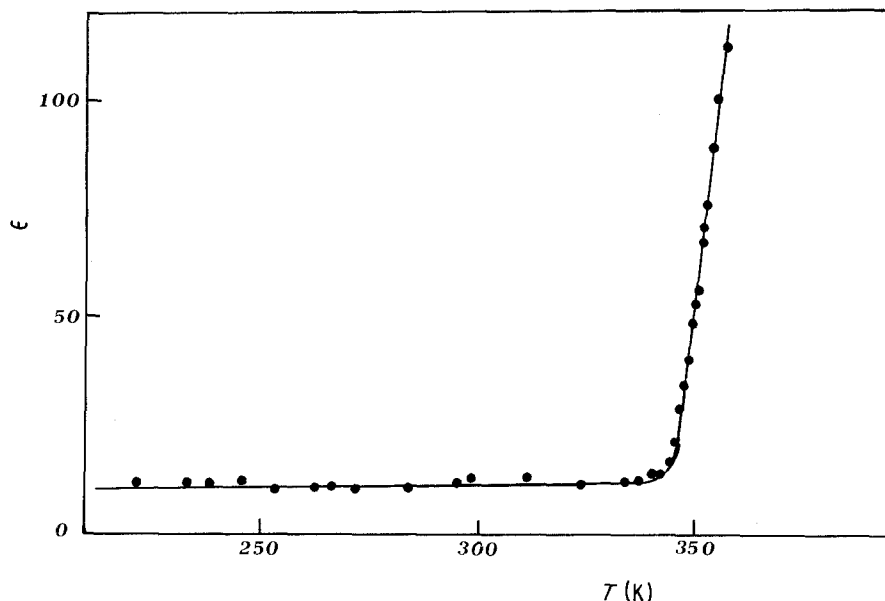


Figure 2 Relation between the dielectric constant and absolute temperature at a frequency of 20 kHz, in $((\text{CH}_3)_2\text{SO})_2\text{FeCl}_2$.

The dielectric constant was measured using the balance bridge [6]. The data were collected at a frequency of 20 kHz in a vacuum cryostat to avoid the effects of moisture.

The a.c. resistivity of the sample was measured at the same time as the dielectric constant.

The magnetic susceptibility of the sample was measured using the conventional Gouy method in which a long tube is filled in a glove box under pure nitrogen gas to avoid oxidation. The data were collected at 1180 Oe while the sample was cooled at different fields of zero, 1820 and 3600 Oe. The temperature range of measurements was from liquid nitrogen temperature up to ≈ 360 K.

The corrected molar magnetic susceptibility as a function of temperature is shown in Fig. 1a. The data were collected from liquid nitrogen temperature up to 330 K. The investigated sample was cooled in different magnetic fields (zero, 1820 and 3600 Oe). The results obtained showed that the cooling fields have no effect on the susceptibility values, because the formation of the ferromagnetic domains due to cooling fields is small or vanishes above T_N . Therefore it is expected

that the Néel temperature [7] of the investigated complex will lie at a temperature lower than the liquid nitrogen temperature. The presence of a small hump around 180 K indicates the short-range magnetic interaction which usually exists in the two-dimensional magnetic systems. From the reciprocal molar magnetic susceptibility curve, Fig. 1b, the value of the Curie constant was found to be 1.94, which gives an effective magnetic moment of $5.49 \mu_B$. This value of the effective magnetic moment agrees nicely with the reported values [8] of Fe^{2+} ions in different symmetry. The value of the Curie-Weiss $\theta = -50$ K indicates the antiferromagnetic character of this compound.

Fig. 2 shows the effect of temperature on the dielectric constant (ϵ) of the investigated compound. From the figure, it can be seen that the dielectric constant (ϵ) remained stable on average from liquid nitrogen temperature up to 300 K, then it increased with increasing temperature. This high-temperature behaviour (from 342 to 360 K) is typical for the simple dielectric material, and it arises from the change in the electronic structure of the crystal lattice. At ≈ 342 K the dielectric constant increases sharply. This sharp change in ϵ

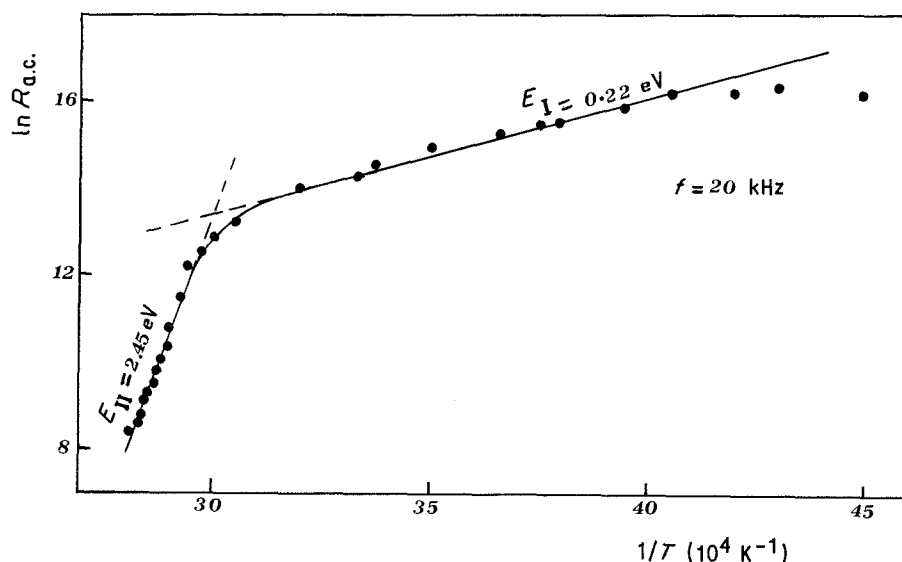


Figure 3 Relation between a.c. resistivity and absolute temperature at a frequency of 20 kHz in $((\text{CH}_3)_2\text{SO})_2\text{FeCl}_2$.

was found to be reversible and is accompanied by a reversible change in the colour of the sample (from yellow to brown). Therefore this change could be attributed to thermochromic phase transition occurring at 342 K. The values of the electric dipole moments below and above the transition point are 1.0×10^{-24} and 9×10^{-24} C m, respectively.

Fig. 3 shows the variation of a.c. resistivity (R) with temperature. From this figure it can be seen that the phase transition, which is shown in the measurements of the dielectric constant at 342 K, is also observed at the same temperature in the measurements of a.c. resistivity. The activation energies obtained from the plot shown in Fig. 3 by applying the Arrhenius equation [9] are $E_I = 0.22$ and $E_{II} = 2.45$ eV for the low- and high-temperature phase, respectively.

The reversible colour change of the sample from the low-temperature phase to the high-temperature phase indicates the presence of reversible phase transition structure. This could be also seen from the experimental data points (ϵ and R) in which a change in coordination geometry around the Fe^{2+} ions, may occur. The change in coordination geometry causes a change in the energy of the electronic transition states lying in the visible region and, in turn, causes the observed thermochromic effect. Similar behaviour was also observed for $(\text{Cu}(\text{DMSO})_2\text{Cl}_2)$ [10] and was

explained on the basis of the results of the temperature dependence of the linewidth of the electronic absorption bands, as due to the presence of a vibrating coupling mechanism for the (DMSO) molecule.

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