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Irradiation Effect on the Electric and Magnetic Properties of Two - Dimensional Organic Complexes

Thesis

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Summary

The present work is concerned mainly with studying the electric and magnetic interaction in diammine complexes $(C_2H)_n(NH_3)MCl_{4-x}Br$, where $n = 3, 6, 9, 12$, $M = Cu^{2+}, Mn^{2+}, Co^{2+}$ and $x = 0, 1, 2$ before and after γ -irradiation with different doses. From the plot of ϵ_r as a function of T , the phase transitions and the polarization mechanisms were identified for each sample. Moreover, from $\ln(\sigma)$ versus the temperature the activation energies at different temperature regions are deduced. Also, from $\ln(\sigma)$ versus frequency, the conduction mechanisms were determined. Graphical representation of dielectric data by means of Cole-Cole (ϵ''/ϵ') at selected temperatures were plotted and the relaxation arc times for most test samples were deduced.

The molar magnetic susceptibility (χ_M) of the complexes under test were measured in the temperature range from 78 K up to 500 K and at different magnetic field strengths (2.10, 2.46, 2.79 kOe) by using Gouy's method. The least square fits for the reciprocal of the molar magnetic susceptibility versus temperature at different magnetic field strengths gave the magnetic parameters [θ , C , μ_{eff} and (J/kB)].

In order to identify the type of charge carriers responsible for the conduction process, the thermoelectric power was measured for the samples using the differential technique in the temperature range (300-500 K).

Before Irradiation the dielectric constant E was found to be affected by varying the length of the hydrocarbon chain embedded between the metallic layers of the complexes. For the complexes $(CH_2)_n(NH_3)_2CoCl_4$; $n = 3, 6, 9, 12$, ϵ_r was found to have larger values for the complexes with odd number of carbon atoms ($n = 3, 9$) than those containing even number ($n = 6, 12$). This is due to the existence of permanent dipoles in the complexes with odd n only. Moreover, it is found that, the complex with $n = 3$ has ϵ_r values larger than those of the complex with $n = 9$, this can be attributed to the difference in the molecular size. While for the complexes with even n , the complex with larger molecule ($n = 12$) has larger electronic polarization component and consequently larger values of ϵ_r .

Also, ϵ_r was found to be affected by varying the metallic ion located at the center of the octahedron. For the complex $NDAMCl_4$, where the divalent metal ion $M = Mn, Co^{2+}$ and Cu^{2+} , ϵ_r decreases with increasing the electronegativity of the divalent metal ion. It is also noticeable that, as the radius of the metallic ion increases, the peak position shifts towards the higher temperature side and the peak values decrease. This was explained in the light of the molecules size and their packing together.

Moreover, ϵ_r was affected by changing the halogen ion. For the complex PDAMnCl_{4-x}Br_x where $x=0, 1$ and 2 , it was found that, ϵ_r increases by increasing x . This was ascribed to the difference in both of the electronegativity and atomic number of the two halides.

The temperature dependence of a.c conductivity, $\ln(\sigma)$, for the complex (CH₂(NH₃)₂CoCl₄; $n=3, 6, 9, 12$, revealed two distinct regions. At the low temperature region (300-390 K), $\ln(\sigma)$ decreases with increasing carbon atoms as a result of decreasing the bridging between layers. While, at the high temperature region (390-500 K), the rotation NH₃ groups between the metallic layers increases and as a result the paths of interaction decrease which increase $\ln(\sigma)$ with increase the carbon atoms.

The effect of changing the divalent metal ion on the temperature dependence of $\ln(\sigma)$ for the complex NDAMCL₄; $M= Mn^{2+}, Co^{2+}$ and Cu^{2+} , shows six distinct regions (I- VI), in the first temperature region I (300-379 K), the conductivity increases by decreasing the ionic radius. In the remainder temperature region (II-VI) (379-520 K), there is no definite general trend for the temperature dependence of $\ln(\sigma)$. Increasing of temperature causes an increase in the lattice dimensions on one hand and weakening the hydrogen bond on the other hand. The first effect results a decrease in $\ln(\sigma)$ while the latter results a increase in $\ln(\sigma)$. It was found also that, the complex containing Cu^{2+} has the highest values of $\ln(\sigma)$ since Cu^{2+} has the largest value of electronegativity compared with to other two metal ions.

For the complex PDAMnCl_{4-x} Br_x ; $x=0, 1$ and 2 , it was found from comparing $\ln(\sigma)$ (a complexes with $x=0$ and $x=2$, that the values of $\ln(\sigma)$ in case of Br⁻¹ ion are larger than those in case of Cl⁻¹. The difference in the electronegativity of the halide behavior of the two ions is the main factor affecting the strength of the H-bond. Also, it was found that, the size of the halide ion plays the major role in the values of $\ln(\sigma)$. However, in the case of complex with $x=1$, $\ln(\sigma)$ generally has values less than those of the complex with $x=2$ and larger than that of the complex with $x=0$. By comparing E_a of the three complexes, one finds that E_a of complex with $x=1$ is the highest one. This is ascribed to the presence of one nonbonding axial Br⁻¹ ion which leads to more structure asymmetry.

Upon determining the influence of changing interlayer separation on the temperature dependence of χ_M for the complex in the form (CH₂)_n(NH₃)₂CoC₄, $n=3,6,9$ at H- 2.10 kOe, it was found that, χ_M for the complex with $n=3$ has the highest values while the complex $n=6$ has the lowest values. As n increases, the distances between with the successive metallic layers increase. This results in a decrease in the ferromagnetic interaction component which in turn increases the antiferromagnetic component and thereby decreases χ_M . Moreover, the complex with $n=6$ which does not contain canted antiferromagnetic behavior has a stronger antiferromagnetic interaction which is responsible for the lowest values of χ_M .

The magnetic susceptibility χ_M of the complex was affected by varying the divalent metal ion. For the complex NDAMCl₄, M= Mn²⁺, Co²⁺ and Cu²⁺, χ_M was measured as a function of temperature and at H = 2.10, 2.46 and 2.79 kOe. It was found that, for the two antiferromagnetic complexes containing metal ions Mn²⁺ and Co²⁺, the complex with Mn²⁺ have χ_M values, larger than those of complex with Co²⁺. This could be attributed the spin quantum number s. In case of the ferromagnetic complex NDACuCl₄, XM has the smallest values since s= 1/2 for Cu²⁺.

The irradiation process causes three different effects in our investigated complexes. the first one is the ionization of the metal ions M²⁺ and change their valency to M³⁺ resulting in a large number of free electrons and thereby increasing In (σ). Moreover, the change of valency is accompanied by a decrease in the ionic radii that result in an additional increase in In (σ). Secondly, it disorders the lattice (i.e. creates lattice defects). each resulting from an ion shift from one site to another. The formation of the lattice defects is reflected as an increase in e and decrease in In (σ). Thirdly, the γ -rays causes rupture of some bonds, thereby decrease or increase the number of electric dipoles per unit volume. This depends on the energy of the γ -dose, if this energy is sufficient to rupture the weak H-bond only it will cause a decrease in the number of dipoles, while if it is enough to rupture the backbone bonds, then the number of dipoles will be increased. The rupture process, leads to an increase in the electrons which in turn increase In (σ).

For the complex PDACoCl₄, ϵ_r values at dose = 3 M Rad lie in between the corresponding values of 1 and 2 M Rad. This could be due to the energy of γ -rays being sufficient to rupture the weak H-bonds and as a result ϵ_r increases are less than the corresponding increases in the case of 2 M Rad At 4 M Rad, the energy of γ -rays becomes capable of breaking the covalent backbone bonds and this in turn increase ϵ_r .

For the complex NDAMnCl₄, the highest values of ϵ_r are obtained at 1 M Rad due to the ionization of Mn²⁺ ion and changing its valency. According to Jahn-Teller theory. this change transforms the symmetric octahedral structure to asymmetric tetragonally distorted octahedron and as a result e increased. As the irradiation dose is increased to 2 and 3 M Rad, ϵ_r decreases and the broad hump observed is divided into two displacive humps at about 376 and 422 K (corresponding to 2 M Rad). This can be explained by considering, the relatively high energy of γ -rays becomes able to break some of the weak H-bonds which decrease ϵ_r . At 4 M Rad, the energy of γ -ray, ruptures the bonds of the hydrocarbon chain, this in turn increase ϵ_r .

For the complex PDACuCl₄, it was found that, ϵ_r increases with increasing the irradiation dose as general trend. The γ radiation ionizes the divalent metal ion Cu²⁺ changing its valency into Cu³⁺, but Cu³⁺ ions in the complex are usually reduced (i.e. become Cu²⁺ ions again by heating), In addition the two

other effects of γ -irradiation mentioned before are still present. At 1 M Rad, the effect of formation of structure defects cancels that of the H-bond rupture and no change in ϵ_r is detected. At higher doses (2, 3 and 4 M Rad), the formation of structure defects become the predominant factor.

From the results of $\ln(\sigma)$ obtained for the irradiated complex PDACOC1₄, it was found that, in the temperature region I (300-335 K). when the complex is irradiated by 1, 2 and 3 M Rad, the first and second effects are present but the ionization effect is the predominant one and therefore, $\ln(\sigma)$ increases by increasing the dose. For the complexes irradiated by 4 M Rad dose, scission of the backbone bonds occurred causing further increase in $\ln(\sigma)$. The same explanation applies to explain the behavior of $\ln(\sigma)$ in the region II (330-445 K) except that, the values of $\ln(\sigma)$ at 3 M Rad dose are slightly lower than the values of $\ln(\sigma)$ at 2 M Rad dose. This may be ascribed to the larger formation of defects, For temperatures above 445 K, $\ln(\sigma)$ becomes thermally activated and as a result increase $\ln(\sigma)$. As the γ -rays dose increases, the probability for the complex to form defects (by heating) becomes lower and as a result $\ln(\sigma)$ decreases by increasing γ -doses.

Comparison between the temperature dependence of $\ln(\sigma)$ for the unirradiated and irradiated complex NDAMnCl₄ shows that, $\ln(\sigma)$ exhibits four different temperature regions (I-IV) with different activation energies. At 1 M Rad, the first effect (ionization of the metal ions) is predominant and so $\ln(\sigma)$ has the highest values. As γ -dose is increased to 2 and 3 M Rad respectively, the second factor (formation of the lattice defects) becomes more effective and thus $\ln(\sigma)$ decreases. At 4 M Rad, $\ln(\sigma)$ increases again. This increase may be due to the increasing of the energy of γ -ray dose which causes rupture of the covalent backbone bonds, which in turn increases $\ln(\sigma)$ again.

The results of effects on $\ln(\sigma)$ for irradiated complex PDACuCl₄ indicated that, $\ln(\sigma)$ is affected by the irradiation doses only in the temperature region (300-375 K). At 1 M Rad, the energy of γ -irradiation is sufficient to ionize Cu²⁺ ions and change their valence to Cu³⁺ and this in turn increases $\ln(\sigma)$. At 2 M Rad, the γ -irradiation forms lattice defects that decrease $\ln(\sigma)$. More increase in the dose of γ -rays (3 and 4 M Rad), caused scission in some backbone bonds and as a result increased $\ln(\sigma)$ again. Beyond 375 K, $\ln(\sigma)$ as a function of T shows no detectable change in its values by irradiation doses. This is ascribed to the fact that, the complex containing Cu³⁺ is unstable and immediately returns to the more stable Cu²⁺ complex. The ionizing effect which is associated with γ -irradiation becomes ineffective in this case. Now, only two remainder effects of the γ -irradiation exist. the first one is the formation of lattice defects which causes a reduction in $\ln(\sigma)$ and the second one is the scission of some bonds which