Electrical Conductivity of some Selected Congo Red-Metal Chelates

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It was established that congo red-metal complexes [(where M = Cr(III), Fe(III), Cu(II), Zn(II), Zr(IV), Th(IV) and UO_2(II)] have conductivities in the range of semiconductors. The energy gap and electrical conductivities depend on the ionic radius, ionic charge on the metal and also on the metal : ligand ratio. The phase transition indicated by the conductivity data are interpreted on the basis of the molecular structure of the congo red.

Organic dyes are the subject of many investigations since they have a variety of applications. The resistance of some dyes such as methyl red, alizarin yellow, brilliant green and congo red are of the order = 10^7 - 10^{11} ohm m [1]. The complexity of dyes makes the formation of several different separated electronic systems possible.

Congo red is a well known azo compound which is used as a direct dye, pH indicator [2-6], corrosion inhibitor in acid media [7] and also it is used for the identification of some cations of rare earth metals [8]. However there are only very few studies regarding relation between the structure of congo red and its electrical conductivity. This study uses electrical conductivity measurements of the solid complexes and spectroscopic techniques and deals with the establishment of the electrical properties of complexes of congo red with Cr(III), Fe(III), Cu(II), Zn(II), Zr(IV), Th(IV) & UO_2(II).

EXPERIMENTAL

The chemicals used in this study were of B.D.H. and Merck pure reagents.

The solid complexes were prepared by mixing a solution of metal chloride, (0.01 or 0.02 M, dissolved in doubly distilled water), and a solution of congo red (0.01 M) in 20 ml of pure ethanol. The mixture was stirred for an hour. The solid complexes separated, filtered, washed several times with doubly distilled water to remove traces of metal ions, finally washed with ether and then dried in vacuum. The purity of samples were checked by thin layer chromatography and also by the method described by Gutmann and Lyons [9,10]. The samples under investigation have a constant R_f value within a given small temperature interval (ΔT), which indicates that the purification of these samples is good enough to carry out the conductivity measurements.

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The finely ground solid was compressed to pellet form of diameter 8 mm and thickness of 2 mm in hydraulic press using up to 5 tons cm^{-2}. The two surfaces were polished, coated with silver paint and checked for good contact. The d.c. conductivity of the samples was measured in the temperature range 350 - 750° K in an evacuated glass cell at constant d.c. voltage using the potential drop method [11]. The temperature of the samples were measured with a digital multimeter (DEL - JAP, HC-5010 EC) using a calibrated Ni-NiAl thermocouple.

A Perkin-Elmer spectrophotometer Lambda 3ß was used to obtain the visible spectra of the ligand and its metal complexes.

RESULTS AND DISCUSSION

Congo red Complexes

The stability constants (pK) of the complexes formed in solution were determined from the results of spectrophotometric measurements by the continuous variation method [13]. The stability constant data in Table 1 reveal that they follow the order:

Th(IV) > Zr(IV) > Cr(III) > Fe(III) > UO_2(II) > Cu(II) > Zn(II).

Electrical conductivity

The electrical conductivity of the congo red and its metal complexes were studied in the temperature range 350 - 750° K. In all cases, the conductivity increased with increasing temperature, indicating that these complexes lie in the range of typical semiconductors [12]. A plot of ln σ *vs* 1/T (σ = conductivity and T is absolute temperature) of the compounds under investigation obeyed the equation $\sigma = \sigma^0 \exp(-E/kT)$, where σ^0 is a constant, E is the conduction energy gap and k is the Boltzmann constant (Fig.1). There is a break in the plot giving two intersecting straight lines suggesting a phase transition.

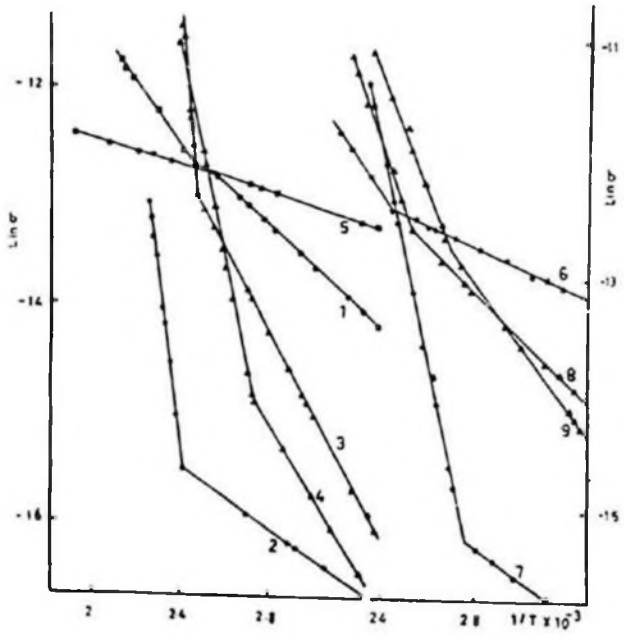
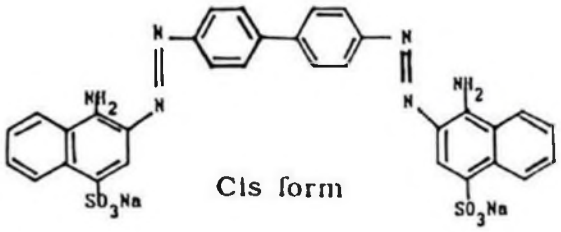


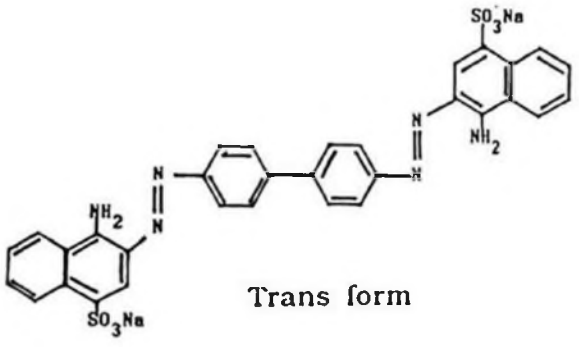
Fig. 1 Electrical Conductivities *vs.* 1000/T of Congo Red complexes.
1. Cr(III) 2. Fe(III) 3. Cu(II) 4. Zn(II) 5. Zr(IV) 6. Th(I:I) 7. Th(I:I) 8. UO_2(I:I) 9. UO_2(2:1)

Phase Transition

The phase transition observed in congo red and its metal chelates may be attributed to the type of packing or the rotation of one azo group relative to the rest of the molecule. Such a rotation results in two molecular configurations - cis and trans.



Cis form



Trans form

At low temperature, the molecules in the ground energy state have a reduced activation energy and increase in their conductivities, so, the trans form is more stable than cis form. By thermal rotation the cis configuration is favoured above the transition temperature. If this is true, one could attribute the phase at low temperature (with low energy gap) to the trnas-form, whereas the phase present at higher temperature to the cis-form.

The phase transition phenomenon was observed in all the complexes and the temperatures of these transitions are listed in Table 1.

Table 1

Measured values of properties of Congo red (L) and its complexes

Specific conductivities (σ in ohm^{-1} cm^{-1}), Activation energies (E in eV),
Transition temperatures (° K),
Wavelength of maximum absorption (max in nm) and Stability constant of complexes (pK)

Compound	σ [10^{-7}]	σ [10^{-5}]	E_1	E_2	T°	λ_{max} nm	pK
L	1.56	0.80	0.29	0.92	360	495	-
Cr:L	7.52	2550	0.12	0.20	385	500,628	10.50
Fe:L	6.82	2.02	0.13	0.34	420	520,668	10.40
Cu:L	1.13	1.21	0.25	0.76	400	485	10.20
Zn:L	1.05	0.75	0.33	0.95	365	472	9.20
Zr:L	9.75	2.35	0.10	0.23	404	552	11.00
Th:L	10.60	1.60	0.09	0.53	410	510,670	11.20
Th_2:L	12.50	2.40	0.08	0.25	490	520,745	11.50
$[UO_2]$:L	1.57	1.85	0.24	0.45	370	490,660	10.10
$[UO_2]_2$:L	7.45	2.80	0.12	0.35	390	-	-

σ_1 is conductivity at 300°K ; σ_2 is conductivity at 400°K

Conduction Energy Gap

The two straight lines with different slopes in Fig. 1 - one before the transition point and the second above - give the two different conduction energy gaps. These are calculated and presented in the Table. It can be noted that the energy gap above transition temperature is higher than the value below this temperature. The change in the type of

packing at transition temperature appears to lead to a change in the singlet - triplet separation.

The observed energy gap below the transition point follow the order Th(IV) < Zr(IV) < Cr(III) = UO_2(II) < Fe(III) < Cu(II) < Cango red < Zu(II). Comparing this with the order of stability constants, it can be noted that conductivity of all complexes increases with the stability of the metal chelates.

It is apparent that the increase of charge on the metal ions decrease the energy gap i.e. the conductivity of the complexes increases. The activation energy of the Zn(II) complex at high temperature is approximatly the same as that of congo red. This indicates that the Zn(II) ion which has no unpaired electrons is similar to congo red. The Zr(IV) and Th(IV) complexes have the lowest energy gap and this is due to the greater charge on the transition metal ions. At higher temperatures, the energy gap of the Zr(IV) complex is lower than that of the Zn(II) complex. The charge of Zr(IV) is greater than that of the Zn(II) although the ionic radius of the two are similar. This means that the charge of ions plays an important role in the conductivity; this increases with increase of charge on the ion.

The energy gap of 1:1 metal complex is greater than that of 2:1 (metal:ligand) complexes both at low and high temperature, i.e. the increase in the ratio of metal ions increases the conductivity of complex. Except zinc-congo red complex, all other complexes studied have energy gaps smaller than that of congo red ligand. These complexes are characterized by an increase in conductivity of the organic ligand owing to the binding with a metal, in which the π-electron systems of the ligand has strong interaction with the valency electrons which leads to an increase in conductivity.

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