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Electrical behaviour of some direct orange complexes

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Abstract

The aim of the present work was to study the effect of complexation on the electrical behaviour of direct orange dye. The composition of the complexes was investigated using IR, XRD and DTA techniques. The conduction mechanism is interpreted on the basis of the band theory. It has been established that the complexes obtained are electronic semiconductors.

INTRODUCTION

There have been intensive studies on the electrical properties of simple organic molecules [1–3]. Naphthalene, considered as a model for pure aromatic compounds, has been studied extensively with somewhat conflicting results [4]. As distinct from ordinary organic compounds, organic semiconductors have noticeable conductivity which in a number of cases (polymers and charge transfer complexes) may approach that of metals (10^{-2}–10^{-4} $\text{ohm}^{-1}\ \text{cm}^{-1}$) at small conduction activation energies [5–7].

In general among the aromatic molecules as a class, conductivity is observed to be higher the larger the molecule. The presence of heteroatoms such as nitrogen or oxygen also appears to enhance the electronic properties including conduction [6]. The organic dyes studied so far seem to fall largely into two classes, the cationic dyes which are n-type semiconductor, and the anionic dyes which are p-type [8].

In a continuation of our recent conductometric studies of the azodye complexes [9], the present work was undertaken in order to elucidate the effect of complexation with Fe^{2+}, Co^{2+} and Ni^{2+} on the electrical behaviour of direct orange dye. In this work, an attempt has been made to characterise the direct orange complexes by plotting their X-ray diffraction patterns in addition to studying their DTA.

EXPERIMENTAL

All chemicals used in the present work were of the highest available purity. The solid complexes were prepared as described previously [9]. The

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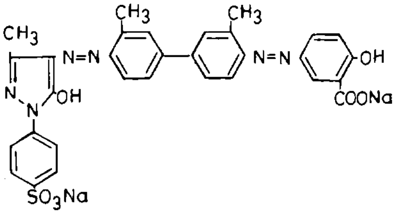
dye has the following structure



The composition of the complexes was studied using IR, XRD and DTA techniques. The IR spectra were recorded on a Pye Unicam SP 2000 infrared spectrophotometer. X-ray diffraction analysis was carried out using a Philips PW 1390 diffractometer with a scanning speed of 1° $\min^{-1}$ and Cu K_α radiation. Differential thermal analysis was carried out under a nitrogen atmosphere using a DT-30 thermal analyser (Shimadzu Co., Japan) with a uniform heating rate of 10 °C $\min^{-1}$.

The electrical conductivity was measured on discs of 10 mm diameter and 3 mm thickness using a Keithley 130 digital multimeter. The method is the same as described elsewhere [9].

RESULTS AND DISCUSSION

The present work is an attempt to determine the molecular structure and electronic behaviour of direct orange azodye and some of its metal complexes. Structural information is provided by a wide variety of physical methods of investigation, the most powerful of which are spectroscopy and diffraction.

The IR spectra of the azodye and of its complexes with Fe^{2+}, Co^{2+} and Ni^{2+} are represented in Fig. 1. The spectra reveal broad bands at 3450 cm^{-1} which are assigned to ν(OH) of the water molecules coordinated to metal ions. This is further supported by the appearance of a broad band at 1650 cm^{-1} corresponding to the deformation mode of coordinated water molecules [10]. The azodye has its ν(N=N) at 1470 cm^{-1} which in complex formation is lowered to 1455 cm^{-1} indicating the coordination of the nitrogen atom of the azo group.

A medium band corresponding to δ(OH) of the free dye is found at 1200 cm^{-1}. It is reasonable to expect a covalent bond between the phenolic oxygen atom and the metal ion on the basis of the broadening of this band and the magnitude of its shift, depending on the metal ion of the complex.

The metal–oxygen and metal–nitrogen stretching frequencies of the compounds under investigation are very interesting, as they are related to the stability and structure of these complexes. The IR spectra of the complexes exhibit several bands in the region 650–200 cm^{-1}. The band near 640 cm^{-1} in the complexes is assigned to ν(M–O) vibration [11]. A new band observed at 410 cm^{-1} is assigned to ν(M–N) [12].

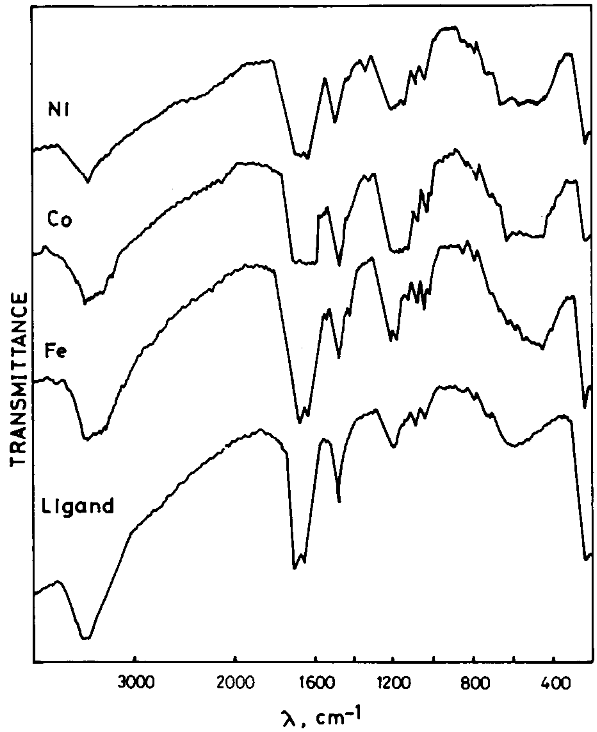


Fig. 1. IR spectra of the direct orange dye and its complexes.

From the change in the infrared spectra, it seems that the bonding between the ions under investigation and the direct orange azodye takes place through a covalent bond with the oxygen atom of the phenolic group and a coordinate bond with the nitrogen atom of the azo group. All the complexes contain two molecules of water of crystallisation.

X-ray diffractometry has been used successfully to analyse the azodye complexes. Table 1 shows the four strongest lines obtained for the organic ligand and its complexes. The results obtained show that:

TABLE 1

X-ray data of direct orange dye complexes

Observations	Azodye		Fe complex		Co complex		Ni complex	
	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
1st strong line	3.9776	0.69	3.9953	0.15	3.9953	0.23	4.0401	0.16
2nd strong line	–	–	3.2433	0.24	3.2433	0.18	3.2725	0.14
3rd strong line	2.8182	1.00	2.8182	1.00	2.8312	1.00	2.8399	1.00
4th strong line	1.9934	0.42	1.9934	0.71	1.9934	0.48	2.0018	0.52

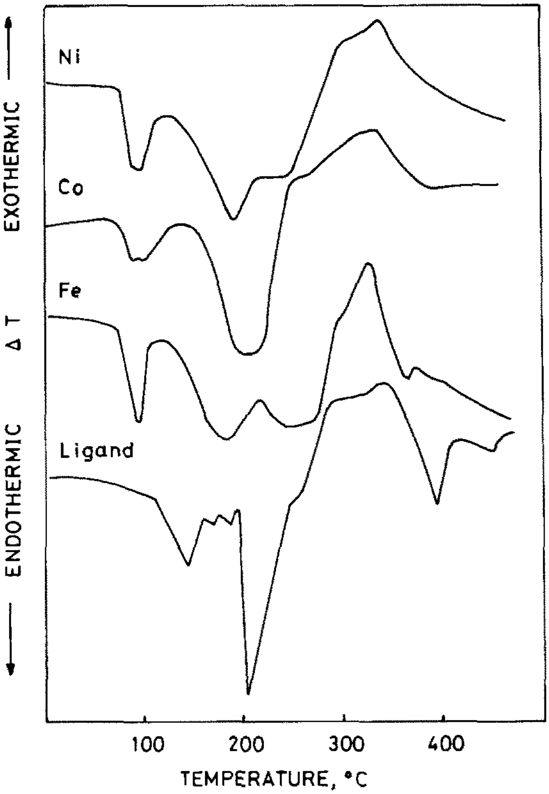


Fig. 2. DTA thermograms of the direct orange dye and its complexes.

1. The intensity of the first strongest line decreases by about 30% after complexation. This is attributed to the interaction of water molecules in the coordination sphere of the complex (M–H_2O).
2. The second strongest line appears only in the metal complexes, indicating that the metal complexes have a defective crystal lattice or a distorted crystalline structure.
3. On complexation, the third strongest line shows a *d*-spacing shift of 0.0217 Å, indicating that the cations are coordinated through the N=N group.
4. The intensity of the fourth strongest line increases on complexation due to formation of an M–O enolic bond.

The XRD results are in a good agreement with the IR data obtained previously.

The influence of exchangeable cations on the nature of the bonding of water molecules in the complex structure has been studied using DTA which charts the changes in energy. The DTA curves of the complexes are shown in Fig. 2. The low endothermic peak at 100 °C is attributed to the expulsion of surface water (physically combined water). The nature of the main

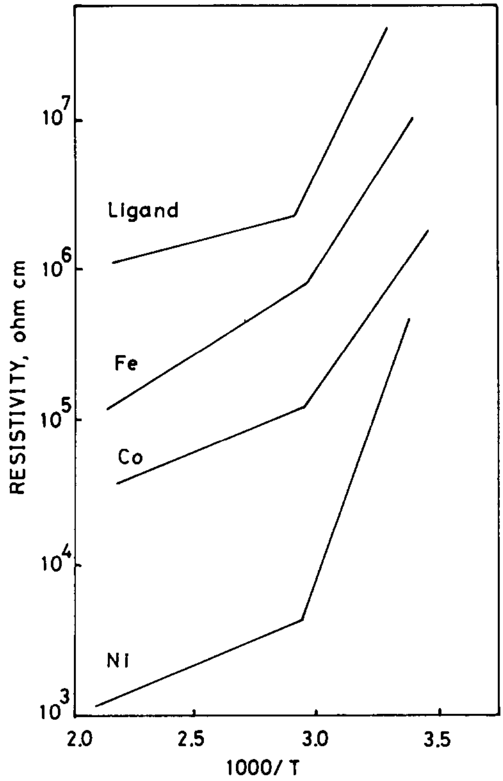


Fig. 3. Electrical resistivity against 1000/T (K) for the direct orange dye and its complexes.

endothermic peak at around 200 ° C which was associated with the expulsion of water from the lattice, remains the same for the various cations, Fe^{2+}, Co^{2+} and Ni^{2+}, but the temperature peaks are slightly different. The exothermic peak at 250 ° C may correspond to the phase transformation of the complexes, while the melting of the complexes is indicated by the peak at 340 ° C. The DTA results indicate that the complexes lose their water of hydration at relatively low temperatures: the step-wise shape as a function of temperature denotes their lower stabilities.

Figure 3 shows a plot of the log of the resistivity against $1/T$ for the three complexes prepared from direct orange dye. The slopes over the temperature range 290–500 K correspond to activation energies of 0.63 eV for the dye and 0.58, 0.49 and 0.80 eV for Fe, Co and Ni complexes, respectively. The resistivities over the measured temperature range are 5.50×10^7, 9.50×10^6, 8.50×10^5 and 2.45×10^5 ohm cm for the investigated compounds respectively, in the range of typical semiconductors. The conjugated system of the dye and the formation of complexes lower the activation energy between the valence state and the next allowed energy state; this could explain the relatively low resistivity of the compounds under investigation.

Previous X-ray analyses of the complexes showed that the dye molecules are stacked after complexation (the second strongest line) with an interplanar distance of 3.24 Å. This value is remarkably smaller than the van der Waals distances in the interplanar spacing between two aromatic ring planes, which are of the order of 7.4 Å. Therefore, the antibonding electron orbitals of the dye, which are perpendicular to the plane of the ring, will overlap and contribute to the electrical conductance.

According to the band theory, semiconduction in organic molecules takes place through the overlapping of molecular orbitals of adjacent molecules. The Π-electron interactions give rise to a conduction zone, common to the entire compound, in which the carrier concentration rises exponentially with temperature. Low mobility is attributed to the narrowness of the conduction bands. According to this mechanism, cations such as Fe^{2+}, Co^{2+} and Ni^{2+} will alter the activation energy of the dye if they influence the mechanism by which the molecular overlap takes place. The results obtained show a clear effect on the activation energy of the dye after complexation.

To calculate the carrier concentration, one can use the relation

$$n = 2\left(\frac{2\Pi m^{+} kT}{h^{2}}\right)^{3/2} \mathrm{e}^{-E/kt} \qquad (1)$$

where m^{+} is the effective mass of charge carrier. The calculation gives n of the order of 10^{14} cm^{-3} for the dye alone and of 10^{10} cm^{-3} for the complexes.

The mobility of the charge carriers μ, was calculated from the conductivity, where

$$\sigma = ne\mu \qquad (2)$$

and e is the charge of an electron. μ is of the order of 10^{-4} cm^{2} V^{-1} sec^{-1} for the free dye which seems low enough to imply that the mean free paths are shorter than the intermolecular spacings. However, for the complexes the value of μ is of the order of 10^{3} cm^{2} V^{-1} sec^{-1}.

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