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ELECTRICAL PROPERTIES OF SOME BIS-AZODYE COMPLEXES

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ABSTRACT

Infrared, conductivity and Seebeck coefficient have been studied for some bis-azodye complexes. It has been established that the complexes investigated are electronic conductors and that they have an exponential temperature dependence similar to that of normal semiconductors. The conductivity data obtained are interpreted on the basis of the band theory.

INTRODUCTION

In recent years an extensive research effort has been concentrated on organic metal compounds [1]. Compounds which belong to this family typically exhibit conductivities of the order of 200–50 ohm^{-1} cm^{-1} at room temperature [2–4]. High electrical conductivity can occur in a purely organic compound under special chemical conditions [5–8]. Among the most significant is the constraint that a sizeable population of carriers can be energetically accessible at ordinary temperature only if the basis states for conduction consist of extended π-molecular orbitals.

Organic dyes are the subject of much investigation since they have possible practical applications. The resistance of some dyes such as ruby S, Bismark brown, basic fuchsin, eosin bluish, methyl red and alisarin yellow is of the order of 10^9–10^{11} ohm cm [9]. The complexity of dyes makes possible the formation of several different more or less separated electronic systems. Therefore, this study deals with the establishment of the electrical properties of some complexes of bis-azodye with Co(II), Ni(II), Cu(II), La(III) and UO_2(II).

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EXPERIMENTAL

The 1,3-bis(2′,4′-dihydroxyphenylazo)-benzene was prepared according to Shautissen [10]. The structure was characterized on the basis of elemental and IR spectral data. The elemental analysis agreed with the theoretical percentages of C, H and N to about 0.4%.

The M : L and M_2 : L type of solid complexes were prepared by mixing a hot solution of the ligand L (bis-azodye) in dimethylformamide DMF with the metal solutions M in 80% DMF/H_2O mixture. The reaction mixture was refluxed for 1 h in an oil bath and then allowed to cool. The separated solid was filtered off, washed with ether and dried in vacuum.

A Perkin–Elmer spectrophotometer model 598 was used to study the IR spectra of the solid complexes using the KBr disc technique. Conductivity measurements were made on 8 mm diameter and 2 mm thickness discs under vacuum. Discs were prepared under a pressure of 3 ton cm^{-2}. Silver paste was used for the electrical contact. Using this technique, resistivity values could be reproduced within a factor of two. The conductivity cell was the same as described previously [11]. The Seebeck coefficient was measured using a Keithley 610 BR electrometer. The temperatures were measured by means of copper–constantan thermocouples attached to a Northrop K-3 potentiometer.

RESULTS AND DISCUSSION

Infrared data

Infrared spectrophotometry is a very useful tool for studying the structure of the solid complexes. Figure 1 shows the IR spectrum of the bis-azodye ligand. The broad band between 3500 and 3450 cm^{-1} can be assigned to the stretching vibration of the phenolic OH group. The two bands at 3070 and 2800 cm^{-1} may be attributed to νC–H stretching in the benzene rings. The band at 2020 cm^{-1} can be assigned to νC=N stretching. The important bands are given in Table 1.

When the bis-azodye ligand is coordinated to the metal ion, the ligand vibrating system, bond lengths and angles as well as inter-atomic forces within the ligand would be expected to alter, as shown in Fig. 1. In comparison to that of the ligand, in the region of νOH, the spectra of complexes exhibit a broad band near 3400 cm^{-1} which may be attributed to νOH of the water molecules associated with the complex formation. Support for this conclusion is given by the presence of a new band in the region 850–800 cm^{-1}. The bands at 1280 cm^{-1} and 1480 cm^{-1} in the spectrum of the free ligand are shifted to lower frequencies indicating that the C–N and N=N groups form one of the coordinating sites in complex formation. Two

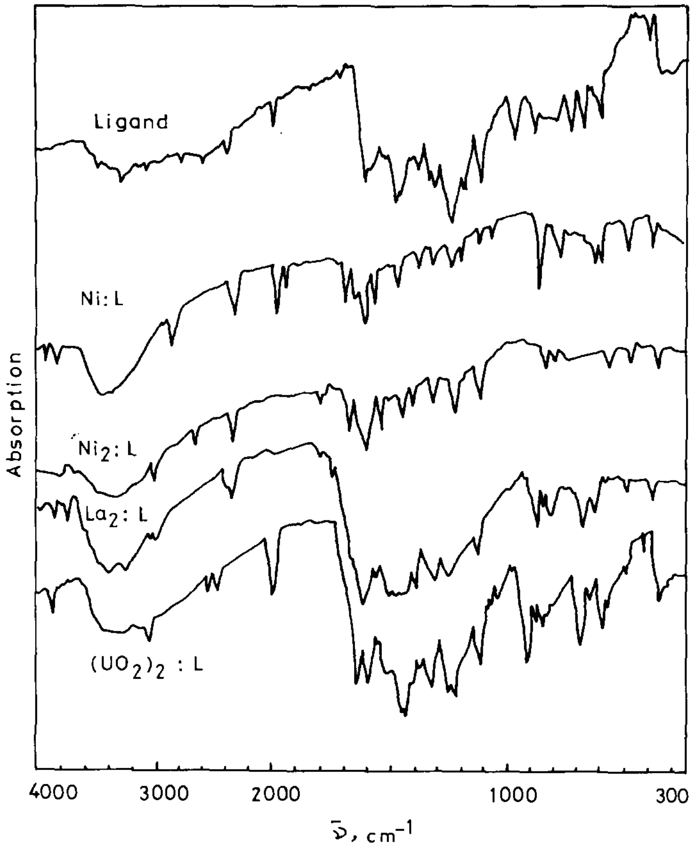


Fig. 1. Infrared spectra of bis-azo complexes.

TABLE 1

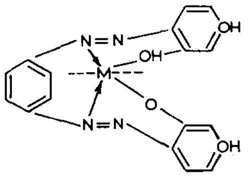
Infrared bands of the bis-azo compound

Frequency (cm^{-1})		Assignment
3450–3500	broad	νOH of phenolic group
3070 & 2800	m	νC–H of benzene rings
2070	m	νC=N
1860–1730	s	δC–H out of plane
1700–1620	s	νC=C
1480	w	νN=N
1315	m	δOH in plane
1280	s	νC–N stretch
1240 & 1125	s	νC–OH
690– 800	m	δC–H bending

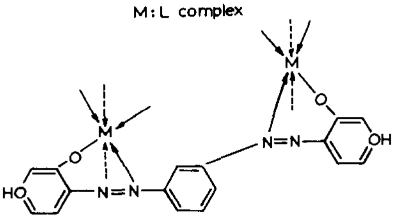
w, Weak; m, medium; s, strong.

new bands appear at 490 and 380 cm^{-1} in the spectra of complexes, which can be attributed to the $\nu M–O$ and $\nu M \leftarrow N$ respectively.

According to the above discussion the following structures of bis-azodye complexes may exist



M:L complex



M_2:L complex

Electrical data

In an attempt to interpret the electrical data of bis-azodye complexes, the logarithm of resistivity has been plotted against the reciprocal of absolute temperature. According to the band theory these plots should yield straight lines over the temperature range 300–450 K, obeying the equation $\rho = \rho^0 \exp(E/kT)$, where ρ is the specific resistivity at absolute temperature T, ρ^0 is a constant, E is the activation energy of conduction and k is the Boltzmann constant. The values computed for ρ, ρ^0 and E are reported in Table 2.

The measured temperature dependences of the electrical resistivities are shown in Fig. 2. The bis-azo compound gives a linear relation which indicates that it behaves like typical intrinsic semiconductors. On the other hand, the phase transition phenomenon was observed in all the complexes investigated. These phase transitions may be attributed to a change in the type of packing which leads to a change in the singlet–triplet separation energy. This can be seen from the relatively high activation energy of conduction obtained above the transition temperature.

The observed resistivities at room temperature of the complexes investigated follow the order $La > UO_2 > Cu > Ni > Co$. It is apparent that increasing stability of the complexes which are formed will decrease the number of dislocated electrons and increase the resistivity. The data ob-

TABLE 2

Resistivities, activation energies and transition temperatures of bis-azo complexes at 300 K

Sample	ρ (ohm cm)	ρ^0 (ohm cm)	E_1 (eV)	E_2 (eV)	T (K)
Ligand	1.95×10^7	74.1400	0.14	–	–
Co : L	3.10×10^6	0.8100	0.17	0.21	363
Ni : L	7.10×10^6	0.1300	0.20	0.24	368
Cu : L	7.30×10^6	4.7100	0.16	0.20	393
UO_2 : L	9.40×10^6	0.0280	0.22	0.28	395
La : L	1.10×10^7	0.0023	0.25	0.32	410
Co_2 : L	3.30×10^6	75.6000	0.12	0.14	378
Ni_2 : L	6.40×10^6	143.2800	0.13	0.16	363
Cu_2 : L	6.38×10^6	142.8300	0.12	0.14	368
$(UO_2)_2$: L	5.10×10^6	280.2600	0.11	0.14	368
La_2 : L	1.10×10^7	0.2000	0.20	0.25	403

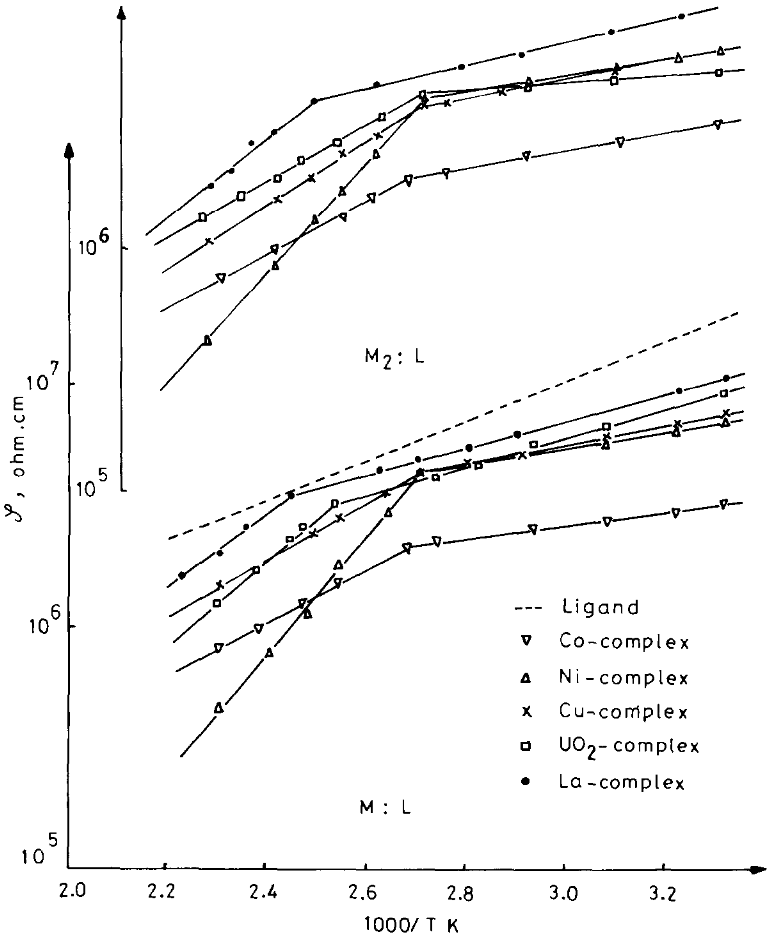


Fig. 2. Electrical resistivity vs. $1000/T$.

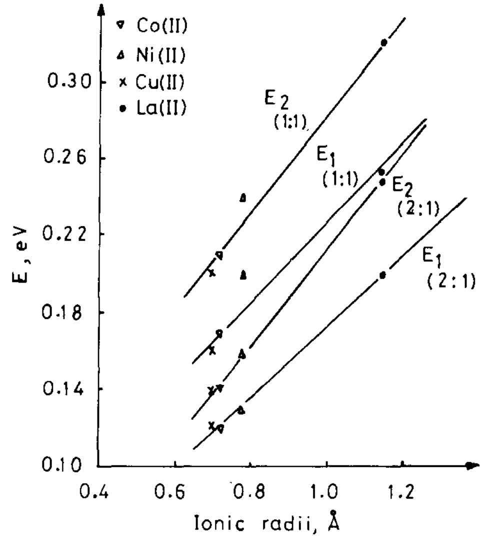


Fig. 3. Activation energy E vs. ionic radii of cations.

tained in this work are in a good agreement with this observation. Only the UO_2 complex does not obey this rule. The uranyl complex is found to be relatively less stable than those of the other cations. This might be due to the difference in the configuration between uranyl on one hand and Co, Ni, Cu and La complexes on the other. The trend of resistivity depends more on the ionic radius of the cation than on its ligand field strength. Figure 3 illustrates that the activation energy E increases linearly with increasing radii of cations (Co^{2+}, 0.72 Å; Ni^{2+}, 0.78 Å; Cu^{2+}, 0.7 Å; UO_2^{2+}, 0.8 Å; La^{3+}, 1.15 Å). Also, E decreases with the complexation, i.e., $E_{1:1} > E_{2:1}$.

According to Table 2 the activation energies of the 1 : 1 complexes investigated are larger than that of the bis-azo compound. This could be attributed to the interaction between the electrons in *d* orbitals of the cations and the anti-bonding π orbitals of the bis-azodye. This interaction will localize the π electronic charge on the ligand, i.e., the energy required for excitation of the localized π electron will increase.

The above results may be rationalized in light of the band theory. One of the valuable aspects of the band theory lies in its success in providing a unified mathematical approach for both inorganic and organic semiconductors. It postulates that semiconduction in organic compounds takes place through the overlapping of molecular orbitals of neighboring molecules. The orbital overlap can arise from excitation of a molecule to the triplet state. Therefore, if the cations (Co^{2+}, Ni^{2+}, Cu^{2+}, UO_2^{2+} as well as La^{3+}) are present as impurities, then they will alter the activation energy of conduction only if they conduct through a similar mechanism. The results obtained in

Table 2 indicate that a significant effect on the activation energy is exerted by the complexation of the bis-azodye with different cations.

Measurements of conductivity alone are not sufficient for determination of both the number of conducting charge n and their mobility μ. Neither do they permit determination of the sign of the predominant charge carrier. However, measurement of the Seebeck coefficient supplies the additional information required. The concentrations of electrons and holes n are calculated from

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

where m^{+} is the effective mass of charge carrier (assumed to be equal to the rest mass of electron) and h is Planck's constant. The conductivities σ are equal to

$$\sigma = en(\mu_{\mathrm{h}} + \mu_{\mathrm{e}}) = en\mu_{\mathrm{h}}(1 + c)$$

where e is the charge of electron, μ_{h}, μ_{e} are the mobilities of holes and electrons respectively and c is the mobility ratio. According to Johnson and Lark-Horowitz [12], the Seebeck coefficient was related to the mobility ratio through

$$Q = -\frac{k}{e}\left(\frac{c-1}{c+1}\right)\left(\frac{E}{kT} + 2\right)$$

The temperature dependence of Q follows the prediction of any simple model. The calculated mobility ratio c ranged from 0.68 to 0.76 indicating electronic carriers to move less freely than holes. A positive Seebeck coefficient Q could arise in intrinsic semiconductors in which $\mu_{\mathrm{h}} > \mu_{\mathrm{e}}$. To illustrate that the conductivity in the investigated complexes is electronic, a sufficient current was passed through a representative sample, Ni : bis-azodye, for two days in order to polarize every C, H, O or N in the sample. However, the resistivity of the sample did not change during this period, i.e., the conductivity must be electronic.

In order to determine the density of states, N, the following relation is used

$$n = N \exp(-(E_{\mathrm{f}} - E_{\mathrm{v}})/kT)$$

where $E_{\mathrm{f}} - E_{\mathrm{v}} = QT$ [13]. The characteristic electrical data of the bis-azo complexes are collected in Table 3. The mobilities are very low which is typical of organic semiconductors. Some of the mobilities are as low as $10^{-12}\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$.

The above elementary discussion suggests a simple model in which the high-temperature treatment serves only to increase the number of states available for conduction. It may also be concluded that there is a correlation

TABLE 3

Electrical properties of bis-azo complexes

Sample	n (cm^{-3})	μ ($cm^2\ V^{-1}\ s^{-1}$)	Q ($mV\ ^{\circ}C^{-1}$)	QT (eV)	N (cm^{-3})
Ligand	1.11×10^{23}	2.89×10^{-12}	0.53	0.16	5.44×10^{25}
Co : L	3.45×10^{22}	5.84×10^{-11}	0.56	0.17	2.50×10^{25}
Ni : L	1.08×10^{22}	8.15×10^{-11}	0.51	0.15	3.60×10^{24}
Cu : L	5.10×10^{22}	1.68×10^{-11}	0.48	0.14	1.15×10^{25}
UO_2 : L	5.00×10^{21}	1.33×10^{-10}	0.61	0.18	5.31×10^{24}
La : L	1.56×10^{21}	3.64×10^{-10}	0.67	0.20	3.59×10^{24}
Co_2 : L	2.40×10^{23}	7.89×10^{-12}	0.50	0.15	8.00×10^{25}
Ni_2 : L	1.63×10^{23}	5.99×10^{-12}	0.48	0.14	3.68×10^{25}
Cu_2 : L	2.40×10^{23}	4.08×10^{-12}	0.46	0.14	5.42×10^{25}
$(UO_2)_2$: L	3.50×10^{23}	3.50×10^{-12}	0.33	0.16	1.71×10^{26}
La_2 : L	1.08×10^{22}	5.26×10^{-11}	0.65	0.20	2.49×10^{25}

between resistivity vs. temperature behavior and the structure of bis-azo solid complexes.

REFERENCES

1 J. Martinsen, J.L. Stanton, R.L. Greene, J. Tanaka, B.M. Hoffman and J.A. Ibers, J. Am. Chem. Soc., 107 (1985) 6915.
2 A.J. Epstein, S. Etemad, A.F. Carito and A.J. Heeger, Phys. Rev. B, 5 (1972) 952.
3 A.N. Bloch, D.O. Cowan, K. Bechgaard, R.E. Pyle, R.H. Banks and T.O. Poehler, Phys. Rev. Lett., 34 (1975) 1561.
4 Y. Tomkiewicz, International Conference on Organic Conductors and Semiconductors, Siòfak, Hungary, 1976, p. 417.
5 M.H. Cohen, J. Non-Cryst. Solids, 2 (1970) 432.
6 I.F. Schegolev, Phys. Status Solidi A, 12 (1972) 9.
7 A.F. Garito and A.J. Heeger, Acc. Chem. Res., 7 (1974) 232.
8 A.J. Berlinsky, Contemp. Phys., 17 (1976) 331.
9 Ch. Ivanova and V. Peneva, International Conference on Organic Conductors and Semiconductors, Siòfak, Hungary, 1976, p. 647.
10 H.A. Schautissen, J. Am. Chem. Soc., 55 (1933) 45355.
11 M.G. Abd El Wahed and A.K. Abd El Kader, J. Mater. Sci. Lett., 4 (1985) 976.
12 V. Johnson and K. Lark-Horowitz, Phys. Rev., 92 (1953) 226.
13 W. Shockley, Electrons and Holes in Semiconductors, Van Nostrand, New York, 1950.