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Structural and Electrical Studies of Coordination Compounds of [1-(2, 4-Dihydroxy-Phenyl)-Ethanone-2-(4-Methylphenyl)-2-Phenylethylamine]

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ABSTRACT

Coordination compounds of transition metals are of particular interest to inorganic chemists because of their structural and chemical properties are often strongly dependent on the nature of the ligand structure. Coordination complexes with substituted ketones have shown diverse structural and properties generating a variety of stereochemistry and a wide range of bonding interactions. Complex formation of many organic compounds plays an important role in the field of conduction. An increase in the conductivity values is observed when metal ions are incorporated into the π electron delocalization of the organic compound. The reduction of conduction is noted if localized bond between metal ions and organic compound is created. In the present study the ligand [1-(2, 4-dihydroxy-phenyl)-ethanone-2-(4-methylphenyl)-2-phenylethylamine] (DHPEMPA) was prepared in ethanolic medium by the reaction of [1-(2,4-Dihydroxy-phenyl)-ethanone] (DHPE) with [2-(4-methylphenyl)-2-phenylethylamine] (MPA) under reflux. The complexes of this ligand have been prepared using metal acetates of Mn(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II) and Cd(II) under reflux in ethanol/DMF. The products were found to be crystalline solid. The ligand and its complexes have been characterized by FT-IR, ^{1}HNMR, diffused reflectance and elemental analysis. The solid state d.c. electrical conductivity of all the compounds have been measured over 313 – 403 K. It was found that the metal complexes exhibit a conventional semiconducting behavior where conductivity shows increasing tendency by raise of temperature. The lower temperature range is the region of extrinsic semiconductors while the upper temperature range attributed to the intrinsic region where carrier is thermally activated from the valence band to conduction band.

1. Introduction

One of the most important problems of present day chemistry is the creation of new substances and materials possessing a series of valuable properties. Particularly great prospects have been opened up in the synthesis and study of organic compounds having delocalized electrons because of the presence of conjugated bonds in them or the formation of complexes**.** Such compounds have acquired the name, organic semiconductors [1].

Inorganic semiconductors stand on the threshold of a bright and exciting future. An organic semiconductor can be synthesised with the properties comparable to those exhibited by inorganic semiconductor materials, such as the development for transistors and the wide array of now existing derivative devices and components of electronics industry [2]. Semiconducting metal complexes constitute one of the most fascinating recent research topics deeply involving both chemists and solid state physicists. Because of the fundamental and technological reasons, considerable interest has been shown in the synthesis and study of organic solids and metal complexes which behave like semiconducting materials. Here we report the synthesis and electrical conductivity of Mn(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II) and Cd(II) complexes of Schiff base ligand DHPEMPA.

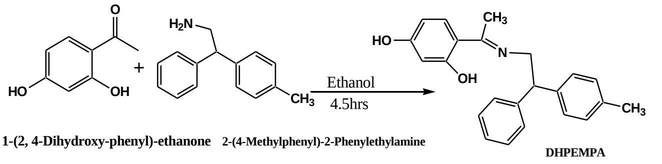
2. Experimental Methods

2.1 Materials

Mn(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II) and Cd(II) acetate salts used were of Merck and BDH make. Organic solvents such as absolute ethanol, methanol, petroleum ether, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were of AR grade. [1-(2, 4-Dihydroxy-phenyl)-ethanone] was prepared by known methods. The solvents were purified by standard methods. Elemental microanalysis was performed on a CHN analyser from heraeus (Vario EL). The chloride contents for complexes were determined by using titration method on 686-Swiss potentiometer. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000 cm^{-1}. ^{1}H-NMR spectrum of the ligand was recorded in DMSO-d6 on a Bruker DRX-300 FTNMR spectrometer. The diffuse reflectance spectra of the complexes were recorded on Varian Cary-5000 UV-visible spectrophotometer. The magnetic moment measurement were made on a Gouy balance at room temperature using [HgCo(SCN)$_4$] as the calibrant. Solid-state electrical conductivity of complexes was measured in their compressed pellet forms using conventional two-probe method.

2.2 Synthesis of 1-(2,4-Dihydroxyphenyl)Ethanone-2-(4-Methylphenyl)-2phenylethylamine [DHPEMPA]

The ligand DHPEMPA was synthesized by condensation of [1-(2, 4-Dihydroxy-phenyl)-ethanone] with 2-(4-Methylphenyl)-2-Phenyl-ethylamine by taking ethanol as a solvent. The reaction scheme can be represented as following Scheme 1.



Scheme 1 Synthesis of DHPEMPA

2.3 Synthesis of Metal Complexes

All the complexes were synthesized by mixing a ethanolic solution of M(CH$_3$CO)$_n$ *n*H$_2$O with the ethanolic solution of Schiff base DHPEMPA in a

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1:2 molar ratio. The resulting mixture was refluxed on a water bath for 7–9 hours. A colored product appeared on standing and cooling the solution. The complexes were filtered, washed with petroleum ether and dried under reduced pressure over anhydrous $CaCl_2$ in desiccators. They were further dried in an electric oven at 60–70 °C.

3. Result and Discussion

The synthesized complexes are colored, stable and non-hygroscopic solids and are insoluble in water, ethanol and methanol but soluble in DMF and DMSO.

3.1 Elemental Analysis

The analytical data indicate 1:2 metal to ligand stoichiometry for all the complexes**.** All the complexes are found to be non-electrolytes. The colors, magnetic susceptibilities as well as the percentage composition of the constituent elements are reported in Table 1.

Table 1 Analytical data of DHPEMPA and its Complexes

S.N.	Compounds	Solvent used	Color	Reflux (hrs.)	Elemental analyses % found (cal.)			
					M	C	H	N
1.	DHPEMPA	EtOH	Dark red	4.5	--	75.02 (75.27)	6.22 (6.71)	5.78 (5.49)
2.	$[Mn(DHPEMPA)_2(H_2O)_2]$ $2H_2O$	EtOH	Golden brown	3.5	8.50 (8.64)	60.98 (60.47)	6.28 (6.34)	4.50 (4.41)
3.	$[Co(DHPEMPA)_2(H_2O)_2]$	EtOH	brown	3	9.87 (9.76)	63.73 (63.68)	6.09 (6.01)	4.70 (4.64)
4.	$[Ni(DHPEMPA)_2(H_2O)_2]$	EtOH	Reddish brown	4	9.82 (9.73)	63.74 (63.70)	5.99 (6.01)	4.58 (4.64)
5.	$[Cr(DHPEMPA)_2(H_2O)_2]$ H_2O	DMF-EtOH	Golden buff	3	8.54 (8.46)	62.48 (62.53)	6.18 (6.23)	4.60 (4.56)
6.	$[Cu\ (DHPEMPA)_2]2H_2O$	DMF-EtOH	Copper leaf	3.5	10.39 (10.45)	63.29 (63.20)	6.02 (5.97)	4.56 (4.61)
7.	$[Zn(DHPEMPA)_2]$	EtOH	Red buff	3	11.46 (11.39)	66.80 (66.96)	5.71 (5.62)	4.93 (4.88)
8.	$[Cd(DHPEMPA)_2]$	EtOH	Red buff	3	18.23 (18.10)	61.74 (61.89)	5.27 (5.19)	4.62 (4.51)

3.2 ^{1}HNMR spectrum of DHPEMPA (300MHz, $CDCl_3$, δ in ppm)

The ^{1}H NMR spectrum of ligand DHPEMPA has been recorded in $CDCl_3$ and is depicted in which indicated that different non- equivalent proton resonates at different values of applied field. These are discussed below: 12.67 (1H, s, phenolic –OH), 7.64-6.6.37 (12H, m, Aromatic protons), 2.32-2.37 (2H, t, protons attached to Nitrogen), 2.19 (3H, s, $-CH_3$), 2.35 (3H, s, $-CH_3$ group present on benzene ring).

Table 2 Infrared absorption frequencies (cm^{-1}) of ligand DHPEMPA and its complexes

S. No.	Compounds	ν(O-H)/ ν(OH-N)	ν(C=N)	ν(C-O)	ν(M-N)	ν(M-O)	H_2O
1.	DHPEMPA	3237	1625	1290	--	--	--
2.	$[Mn(DHPEMPA)_2(H_2O)_2]2H_2O$	--	1595	1375	510	460	3212, 1532, 827
3.	$[Co(DHPEMPA)_2(H_2O)_2]$	--	1603	1387	514	490	3222, 1512, 840
4.	$[Ni(DHPEMPA)_2(H_2O)_2]$	--	1591	1360	525	470	3329, 1538, 820
5.	$[Cr(DHPEMPA)_2(H_2O)_2]H_2O$	--	1596	1367	520	457	3300, 1511, 834
6.	$[Cu\ (DHPEMPA)_2]2H_2O$	--	1580	1350	526	485	3439
7.	$[Zn(DHPEMPA)_2]$	--	1592	1325	521	488	---
8.	$[Cd(DHPEMPA)_2]$	--	1590	1320	578	470	---

3.3 Infrared Spectral Analysis of Schiff Base Complexes

In all complexes, the band for azomethine group undergoes a shift to lower energy, indicating coordination of azomethine nitrogen with metal ion [3, 4]. This fact is further supported by appearance of some new bands ν(M–N) at 510-578 cm^{-1} and ν (M–O) at 457-490 cm^{-1} in the spectra of complexes [5]. In the complex broad band from 3200 to 3600 cm^{-1} may be assigned to presence of lattice water. In addition to above bands, the IR bands due to phenyl ring systems between 1520 and 1566 cm^{-1} which are almost unaffected in the complex have been assigned to aromatic ν(C=C). In all complexes the band for phenolic (C–O) stretching shows a marked shift of 17–25 cm^{-1} to higher wave number due to the C–O–M bond formation [6]. The band for intramolecular H bonding is absent in complexes indicating deprotonation of phenolic –OH group and coordination with metal. Bands at 820-850 cm^{-1} may attribute to rocking and wagging modes of the coordinated water. This band is absent in the spectra of CuL, ZnL and CdL indicating absence of coordinated water. It is concluded from the significant shift of free ligand ν(C=N) to lower wave number side, increased wave number for phenolic ν(C–O) stretching band in complexes, that bonding of the ligand to metal ion is through phenolic oxygen and azomethine nitrogen. The data of IR is tabulated in Table 2.

3.4 Electrical Conductivity

The DC electrical conductivity of Mn(II), Co(II), Ni(II), Cr(III), Cu(II), Zn(II) and Cd(II) complexes have been studied in the temperature range 313 – 403 K using the two probe technique. The general behavior of electrical conductivity obeys the relation,

$$\sigma = \sigma_0 \exp(-Ea/kT)$$

Where σ_0 is a constant, Ea is the activation energy of conduction process, T is the absolute temperature and k is the Boltzmann constant. The electrical conductivity of the complexes at 373K lies in the range of 6.25×10^{-11} to 3.17×10^{-11} Ω^{-1} cm^{-1}. The activation energy of the complexes lies in the range 0.387-0.779 (Table 3). The observed low value of electrical conductivity may be attributed to low molecular weight due to which the extent of conjugation becomes low or undesirable morphology due to pressing of the sample into hard brittle pellet form. It was observed that ΔE values decreases and the conductivity increases comparing to that of free ligands, this may be due to the overlap between the electrons in the antibonding π orbitals of ligand, the empty d-orbitals of the transition metal cation. It leads to delocalization of the π electronic charges on the molecules [7-10].

Table 3 Electrical conductivity data of DHPEMPA complexes

S.N.	Compound	Assignments	Electrical conductivity (Ω^{-1} cm^{-1}) at 373 K	Activation energy (eV)
1.	$[Mn(DHPEMPA)_2(H_2O)_2]$ $2H_2O$	$^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(^4G)$ $^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g(^4G)$	4.27 x 10^{-10}	0.779
2.	$[Co(DHPEMPA)_2(H_2O)_2]$	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	3.60x10^{-11}	0.387
3.	$[Ni(DHPEMPA)_2(H_2O)_2]$	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	4.05 x10^{-11}	0.638
4.	$[Cr(DHPEMPA)_2(H_2O)_2]H_2O$	$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$	3.17 x10^{-11}	0.598
5.	$[Cu\ (DHPEMPA)_2]2H_2O$	$^2B_{1g} \rightarrow {}^2A_{1g}$ $^2B_{1g} \rightarrow {}^2E_g$ C.T.	3.69 x10^{-11}	0.530
6.	$[Zn(DHPEMPA)_2]$	---	3.79x10^{-10}	0.503
7.	$[Cd(DHPEMPA)_2]$	---	6.25 x10^{-11}	0.515

4. Conclusion

The property of electrical conductance is usually employed to study the nature of concerning mechanism of conduction. The d.c. electrical conductivities of metal complexes of Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with the Schiff base ligands used in the present course of study were measured in their compresses pellet form. The activation energies of electrical conductance of all complexes have also been calculated. The complexes in the present study show semiconducting behaviour as their plots of log σ vs. 1/T were found to be linear.

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