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SYNTHESIS AND ELECTRICAL STUDIES OF SOME 1-SUBSTITUTED- 3-FORMAMIDINO THIOCARBAMIDES TRANSITION METAL COMPLEXES

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ABSTRACT

Transition metal complexes from 1-substituted-3-formamidino thiocarbamide with melal ions Ni(II), Co(II), Mn(II), Cu(II), Zn(II) and Cd(II) have been synthesized. The prepared ligand and its complexes were identified by IR, ^{1}H NMR, UV-visible and elemental analysis. These used techniques facilitated to elucidate the chemical structures of the chelates. These techniques show that transition metals form complexes with ligand in the ratio 1:2 [M:L]. D.C. electrical conductivity was measured in pellet form over temperature range 303-498 K.and the activation energy of complexes were also calculated from Arrehenius plots.

Keywords *– Thiocarbamide, Elemental analysis, Electrical conductivity, Activation Energy.*

1. INTRODUCTION

From more than last one decade, there has been a dramatic growth of interest in inorganic complexes materials that exhibit unusual properties. Transition metal complexes have been found to be important precursor for semi conducting materials. Inorganic semiconductors stand on the threshold of a bright and exciting future. An organic semiconductor can be synthesized 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 [1]. 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 [2]. The electrical conductivity of organic compounds is an important physical property. Organic conductors have high number of unsaturated C=C bonds forming conjugated system. It is known that the π-electrons of such system are not bound to definite carbon atoms but are capable of moving the entire molecule. Although a variety of conjugated organic molecules are known to act as semiconductors, carrier mobility in them usually is very low [3,4].

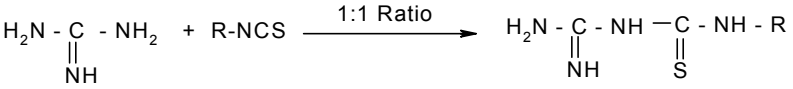
In this contest, the present work describes the synthesis and characterization of some Ni(II), Co(II), Mn(II), Cu(II), Zn(II) and Cd(II) 1-substituted 3-formamidino thiocarbamides complexes. These complexes have been characterized with the help of elemental analysis, infrared and ^{1}H NMR spectra. The coordination complexes have also been studied for their electrical conductivity in pellet form over temperature range 303-498 K.

2. MATERIALS AND METHODS

Nickel(II) acetate tetrahydrate, Cobalt(II) acetate tetrahydrate, Manganese(II) acetate tetrhydrate, Copper(II) acetate monohydrate zinc(II) acetate dihydrate and cadmium(II)chloride monohydrate were obtained from E. Merck. DMF and ethanol were used after distillation. Elemental microanalysis was performed on a (C.H.N) analyzer from heraeus (Vario EL). IR spectra of the compounds were recorded on Shimadzu-FTIR: Affinity 1 spectrophotometer in the region 400-4000cm^{-1}. ^{1}H-NMR was acquired with BRUKER-400 spectrometer in $CDCl_3$ at 300 MHz. The solid state electrical conductivity of complexes was measured in their compressed pellet form by the two-probe method using Zentech resistivity meter in the temperature range 303-498 K[5].

a) Synthesis of ligand

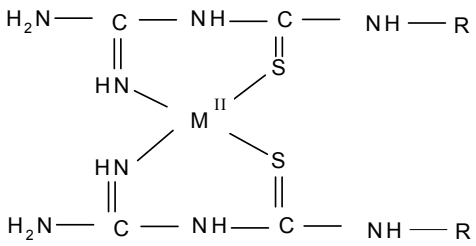
The chosen chelate, 1-substituted-3-formamidino thiocarbamide (PFTC) is rich in electron due to the existence of nitrogen and a sulphur atom is synthesized by following method. The synthesized ligand showed the expected elemental composition and infrared spectra.



R- Phenyl

b) Synthesis of Complex

The synthesis of the complexes is carried out by refluxing 1-substituted-3-formamidino thiocarbamide (PFTC) with Ni(II), Co(II), Mn(II), Cu(II), Zn(II) and Cd(II) metal ions.



3. RESULTS AND DISCUSSION

All the complexes are amorphous powders, found to be insoluble in water and almost all organic solvents. Elemental data confirms the assigned stoichiometries and shows that all the chelates have the general formula ML_2.

IR spectrum of (PFTC) exhibits band at 3330 cm^{-1} which may be assigned to NH stretch, which is shifted to a lower frequency region by 10-20 cm^{-1} in the chelates[6]. The medium strong bond appearing at 2620 cm^{-1} in the free ligand disappears in the chelates and the formation of M-S bond[7]. The spectra of all the chelates show appearance of new bands in the region 410-560 cm^{-1} and 340-360 cm^{-1} indicating M-N and M-S stretching respectively [8]. The broad peak observed around 3400-3500 cm^{-1} is due to υ OH of water molecules. In the spectra of Co(II) chelate, additional peaks in the range1569-1585 cm^{-1} and 700 cm^{-1} have been observed, which is attributed to the presence of coordinated water molecules.

The electrical conductivity of all the chelates was studied over a wide range of temperature. The data reveals a linear trend with inflection appearing at different positions. 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 values of electrical conductivity (σ) lie in the range of typical semiconductor [9]. The logarithm of the conductivity was

plotted against reciprocal of the absolute temperature. All the plots show greater slop in high temperature region while lower activation energy has been observed in lower temperature region.

The metal chelates exhibit a conventional semiconducting behavior where conductivity shows increasing tendency by raise of temperature. The lower temperature range is the region of extrinsic semiconductors where the conduction is due to the excitation of carrier from donor localized level to the conduction band. At the upper temperature range, the intrinsic region is reached where carrier are thermally activated from the valence band to conduction band [10]. This behaviour can be attributed to interaction between the electrons of d-orbitals of metal and π -orbitals of ligand at upper temperature range [11]. This interaction will lead to localized action of π -electronic charge on the ligand which leads to increase the activation energy. On the other hand it is known that increasing of complex stability results in decreasing conductivity due to a decrease in π -electron mobility[12] which agree with obtained results. The activation energy of the chelates decreases in the order Co > Mn > Zn > Ni > Cu > Cd.

Table 1: Analytical data of PFTC and its Complexes

S.N.	Compounds	Time of Reflux (hrs.)	Elemental analyses % found (calcd.)				
			M	C	H	N	S
1.	PFTC	4	--	61.31 (61.44)	4.48 (4.50)	4.11 (4.23)	10.32 (10.54)
2.	$[Ni(PFTC)_2.2H_2O]$	9	14.98 (14.19)	52.12 (52.72)	3.60 (3.87)	3.52 (3.61)	9.27 (9.16)
3.	$[Co(PFTC)_2].2H_2O$	4	14.98 (14.86)	54.75 (53.12)	3.84 (4.27)	3.83 (3.49)	10.02 (10.13)
4.	$[Mn(PFTC)_2.2H_2O]$	4	15.12 (15.02)	52.48 (52.21)	3.98 (3.83)	3.45 (3.58)	9.20 (9.07)
5.	$[Cu(PFTC)_2]$	8	16.28 (16.06)	51.42 (51.57)	3.86 (3.97)	3.42 (3.79)	9.84 (9.96)
6.	$[Cd(PFTC)_2]$	7	14.10 (14.41)	53.55 (53.70)	03.73 (4.06)	3.57 (3.07)	10.01 (10.00)
7.	$[Zn(PFTC)_2]$	7	15.75 (15.57)	51.62 (50.24)	03.84 (4.44)	3.65 (3.16)	10.19 (10.18)

Table 2: Electrical conductivity data of PFTC complexes

S.N.	Compound	Color	Electrical conductivity Ω^{-1} cm^{-1} (K)	Activation energy in eV
1.	$[Ni(PFTC)_2.2H_2O]$	Green	5.05×10^{-5} (373) 3.12×10^{-2} (453)	0.552
2.	$[Co(PFTC)_2].2H_2O$	Off Brown	9.90×10^{-5} (373) 6.38×10^{-2} (453)	0.939
3.	$[Mn(PFTC)_2.2H_2O]$	Pale Orange	8.05×10^{-4} (373) 6.69×10^{-2} (453)	0.888
4.	$[Cu(PFTC)_2]$	Raven Song	6.19×10^{-4} (373) 4.60×10^{-1} (453)	0.548
5.	$[Cd(PFTC)_2]$	Pale Yellow	3.46×10^{-4} (373) 2.67×10^{-2} (453)	0.345
6.	$[Zn(PFTC)_2]$	Yellow	1.13×10^{-3} (373) 1.02×10^{-1} (453)	0.754

4. CONCLUSION

The experimental evidence thus obtained, the Ni(II), Co(II) and Mn(II) complexes were suggested to possess octahedral structures, Cu(II) complex shows square planer and Zn(II) and Cd(II) complexes show tetrahedral structure. These complexes display electrical properties, and show that the conductivities increase with increasing of temperatures which is consistent with semiconductors properties.

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