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Preparative and Structural Studies of Some Transition Metal Polymeric Complexes

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ABSTRACT

This article deals with preparative and structural studies of some transition metal polymeric complexes. The metal polymeric complexes were synthesized from *bis*-ligand with metal salt in dimethylformamide medium by condensation method and their structures have been evaluated by spectral, magnetic moment measurements, X-ray diffraction, thermogravimetric analysis XRD analysis reveals amorphous natures of metal polymeric complexes. Furthermore, scanning electron microscope studies have been performed to determine the shape and size of metal polymeric complexes. The solid reflectance and magnetic moment studies supported significantly tetrahedral geometry for Zn(II), Cd(II) and Hg(II) polymeric complexes. The lattice water was identified by IR, CHN and thermal analysis.

Keywords: Metal polymeric complexes, *bis*-ligand, morphology behaviour, lattice water

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INTRODUCTION

The integration of metal ions into the synthetic polymer chains leads to appropriate a property which creates a new and flexible class of functional materials that improved processability. The presence of the metal considered as the most crucial factor in organometallic molecules because it brings molecular arrangements which are not found in other organic derivatives [1-4]. The organometallic polymers have magnetized significant awareness in the last epoch due to their magnetic, electrical and electrochemical properties [5-6]. However, many researchers have shown that the coordination of organic moieties to a transition element cause have deviation in the biotic activity of organic ligand and metal ion [7-8]. Herein, we have reported a series of transition metal polymeric complexes of aromatic amides *bis* (bidentate) ligand. The tremendous applications of aromatic imides polymers in daily life are due to their excellent physical and chemical properties in the field of optical devices, optical waveguides, lens and optical image sensor [9].

In recent years, most of the works have been done in the synthesis of aromatic polymeric complexes containing silicon because of their potential applications in composite materials, coating, ceramic precursor, optical and semi-conducting materials [10-14]. Fluorine-containing polymers also have variety of applications such as separation membranes, coating, photoresist and medical materials due to their good properties like chemical resistance, good antiweatherbility, low surface energies, UV-stability, low water absorption, good dielectric and optical properties [15]. The aromatic polyamides have high thermal stability, outstanding mechanical strength and good chemical resistance [16,17], but it has some negative effect on electrical insulating and dielectric performance [18]. Similarly polyaniline is also one of the most important conducting and semi-conducting polymers widely used in organic optoelectronic devices and has attracted considerable attention recently because of its electrical conductivity, easy preparation from common chemical and excellent thermal and environmental stabilities [19,20].

The literature survey has reveals that not much more work has been reported on the metal polymeric complexes of isophthalic derivative. This article discusses preparative and structural behaviour of metal polymeric complexes. Furthermore their solid state electrical conductivities were measured in compressed pellet form. SEM studies have significantly helpful to identify difference between morphology of chelating ligand and its metal polymeric complexes.

MATERIALS AND METHODS

Isophthalic acid (SD Fine), Phosphorus pentachloride (SD Fine), p-anisidine (LOBA Chemie), Urea (SD Fine), Benzene (SD Fine), Glacial acetic acid (SD Fine), Dimethyl formamide (E.MERK), Dimethyl sulfoxide (E.MERK), Ethyl alcohol, Dichloromethane(SD Fine), Zinc acetate (E.MERK), Cadmium acetate (E.MERK) and Mercury acetate (E.MERK) were A.R. grade. The chemicals which are used for the synthesis of ligand and its metal polymeric complexes were of analytical grade. The solvents were double distilled before used. Paramethoxyphenylcarbamide was prepared by standard procedure.

Preparation of *bis*-ligand

Isophthaoyl-*bis* (*p*-methoxyphenylcarbamide) ligand was synthesized in two-step process and its physicochemical, spectral characterization was investigated and published [21]. The *bis* (bidentate) ligand was soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) with melting point 355 ^{0}C and yield 72 %.

Synthesis of transition metal polymeric complexes

Synthesis of Zn(II) polymeric complex

Metal polymeric complexes were synthesized from isophthaoyl-*bis*(*p*-methoxyphenylcarbamide) with metal salts [22]. Herein we have prepared zinc polymeric complex by dissolving zinc acetate (0.01mole, 0.219 g) and *bis*-ligand (0.01mole, 0.462 g) separately in 50 ml hot dimethylformamide (*DMF*). The solutions of zinc acetate and ligand were mixed in hot condition and refluxed in an oil bath. The temperature of reaction mixture was maintained 150 ºC. The resulting colored polymeric complex appeared after 20 h. The products obtained were filtered, washed repeatedly with hot dimethylformamide, alcohol to remove unreacted reactant and dried overnight under oven. The obtained product was insoluble in almost all organic solvents and its physicochemical, elemental analysis data have been given in Table 1-2.

Table 1 Physicochemical data of IBPMPC and its polymeric complexes

Polymers	Color	Formula	Formula Wt. %	Yield
IBPMPC	Yellow	$C_{24}H_{22}N_4O_6$	462	72
IBPMPC-Zn	Off white	$(C_{24}H_{26}N_4O_9Zn)_n$	$(579.39)_n$	58.7
IBPMPC-Cd	Yellow	$(C_{24}H_{20}N_4O_6Cd)_n$	$(572.41)_n$	55.3
IBPMPC-Hg	Pale green	$(C_{24}H_{22}N_4O_7Hg)_n$	$(678.59)_n$	53.8

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Table 2. Analytical data of IBPMPC and its polymeric complexes

Polymeric Complexes	% C Obs(Calc)	% H Obs(Calc)	% N Obs(Calc)	% M Obs(Calc)	m.p./ Dec.Temp	Conductivity (Ω cm^1)
IBPMPC	61.9(62.2)	04.4(04.7)	12.4(12.1)	-- --	355	3.3×10^{-7}
IBPMPC-Zn	49.6(49.7)	04.4(04.5)	09.5(09.6)	11.1(11.3)	596	5.9×10^{-10}
IBPMPC-Cd	50.2(50.3)	03.6(03.5)	09.6(09.8)	19.5(19.6)	800	6.3×10^{-11}
IBPMPC-Hg	42.4(42.5)	03.1(03.2)	08.208.3)	29.5(29.6)	700	7.2×10^{-11}

Synthesis of Cd(II) polymeric complex

The reagent solution of *bis*-ligand (0.01 moles, 0.462 g) was mixed in hot condition with cadmium acetate solution (0.01mol, 0.266 g) and refluxed in an oil bath. The yield of colored polymeric product was obtained 55.3 %.

Synthesis of Hg(II) polymeric complex

The reagent solution of *bis*-ligand (0.01 moles, 0.462 g) was mixed in hot condition with mercury acetate solution (0.01moles, 0.318 g) and refluxed in an oil bath. The yield of colored polymeric product was obtained 53.8 %.

CHARACTERIZATION

Spectral analysis and Magnetic moment measurements

IR studies of metal polymers were recorded at Sophisticated Instrumental Facility, Department of Chemistry, Indian Institute of Science Bangalore (India). Solid reflectance spectral analysis was recorded at STIC Cochin University, Kerala, India. IR spectroscopy detects variation in stretching frequency of *bis* (bidentate) ligand and metal polymeric complexes, while UV-reflectance study of polymer predicts the geometry of compounds.. The magnetic moment measurements of polymeric complexes were carried out at room temperature by Gouys method at Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University Nagpur, India.

X-ray diffraction, SEM and Electrical conductivity

X-ray diffraction analyses of metal polymers were carried out at Sophisticated Instrumental Facility, Department of Chemistry, Indian Institute of Science (IISc), Bangalore (India). Electrical conductivity of metal polymeric complexes was carried out in pellet form of solid powder and found an average range of conductivity. The study were carried out in compressed pellet form over 311 K. SEM analyses of polymeric complexes were carried out on scanning electron microscope machine at STIC Cochin University Kerala, India.

RESULTS AND DISCUSSION

Spectral characterization

The infrared spectra of metal polymeric complexes were compared with *bis* (bidentate) ligand to determine the changes that might have took place during complexation. The strong sharp band observed at 3353.99 cm^{-1} in ligand may be due to the N-H group frequency [23-25]. This band shifted toward the lower frequency in polymeric complexes [26]. The N-H group stretching frequency for Zn(II), Cd(II) and Hg(II) were found at 3382.68, 3252.17 and 3442.38 cm^{-1} respectively. The noticeable sharp band was observed at 1668.55 cm^{-1} may be due to the C=O bond in ligand, whereas in polymeric complexes it was shifted at the lower frequency in range 1635.54-1661.98 cm^{-1} due to the weaking of bond [27] . The strengthened of C=N bond was observed as a result of enolization which results in the disappearance of C=O to C-O bond and appearances of C=N from C-N bond in polymeric complexes. The shifting of this band in metal polymeric complexes suggested the covalent coordination bond through oxygen to metal ion. The similar strong band was observed in *bis*-ligand and its polymeric complexes at range

1492-1542 cm^{-1} which may be due to the C=C group frequency of aromatic ring [28] and stretching frequency of 1085-1022 cm^{-1} because of -OCH_3 group [29]. It is noteworthy that the weak bands were found at range 335-557 cm^{-1} and 554-669 cm^{-1} in polymeric complexes due to the metal–oxygen and metal–nitrogen ($M \leftarrow N$) respectively. The stretching frequencies at 3445-3510 cm^{-1} were found in polymeric complexes may be due to the lattice water.

The reflectance spectral studies were helpful for determining the geometry of metal polymeric complexes. The metal polymeric complexes did not showed strong d-d transition however, it showed one weak peak due to the ligand to metal charge transfer spectra (LMCT) and because of this they found colored complexes, and have tetrahedral geometry [30].

X-ray diffraction and electrical conductivity properties

XRD pattern of metal polymeric complexes was obtained in solid form. The morphological structures of metal polymeric complexes have been studied by X-ray diffraction analysis. The X-ray diffractogram of Zn(II), Cd(II) and Hg(II) polymeric complexes showed broad peak, which indicates that amorphous nature. Though amorphous structure of these polymeric complexes, yet they do not soluble in common organic solvents. The electrical conductivities measured in compressed pellet form over 311 K of all metal polymeric complexes have tabulated in Table 2 which were found an average range of $7.2 \times 10^{-11} – 3.3 \times 10^{-7}$ Ω cm^{-1} which indicates the low level of semiconductor nature.

Morphological behaviour (SEM)

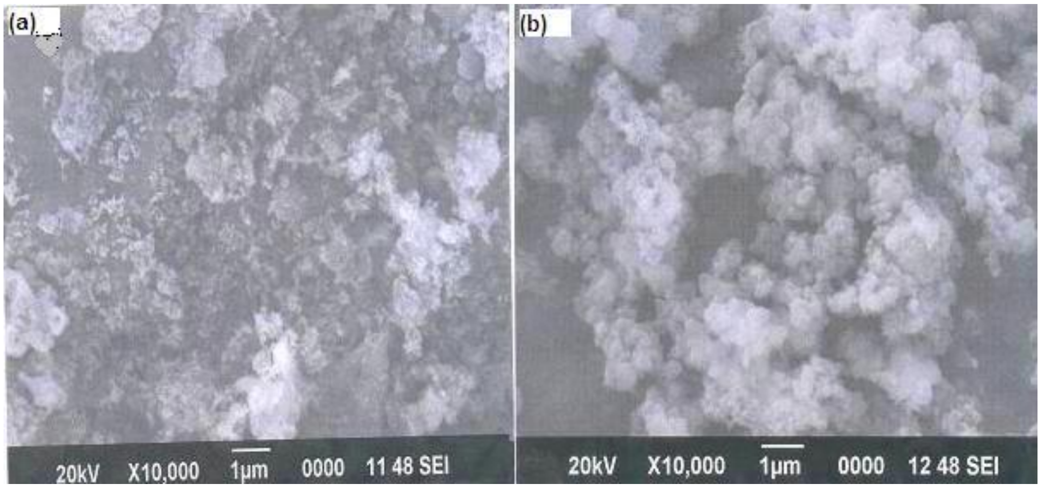

Fig. 1. SEM image of Zn(II) and Cd(II) polymeric complexes

This technique is noteworthy helpful to study the morphology of ligand and polymers. The morphology of Zn-polymeric complex (Fig. 1) was appeared as rock like structure having number of patches on surface, this reveals amorphous nature. It was complicatedly interpreted due to the unclear appearance. SEM image of Cd-polymer (Fig. 1) shows somewhat beads shape and number of beads stack on each other, hence it forms cotton shape look. Scanning electron microscopy image of Hg(II) observed similarity with Cd-polymer.

CONCLUSIONS

Here we have reported preparative and structural studies of metal polymeric complexes of *bis*-ligand. Newly synthesized metal polymeric complexes were coloured and insoluble in all common organic solvents. The presence of hydration water was identified by CHN, IR and thermal analysis. On the basis of the elemental data, spectroscopic studies, UV-reflectance, magnetic susceptibility measurements and X-ray diffraction studies it has been found that the ligand coordinate to central metal ions through oxygen and nitrogen and have tetrahedral geometry for Zn(II), Cd(II) and Hg(II) polymeric complexes. The proposed structure for metal polymeric complexes have shown in Fig.2

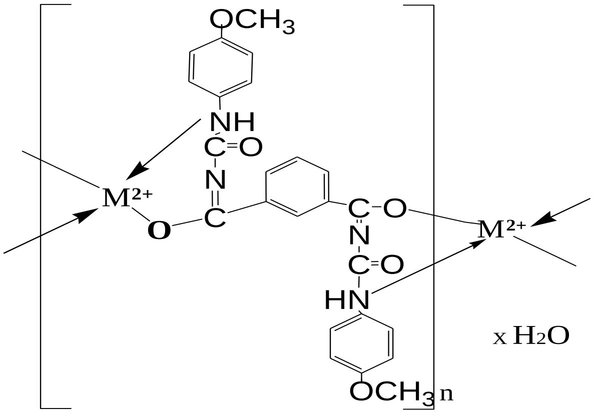

Fig.2. The proposed structure of metal polymeric complexes of isophthaoyl-*bis* (*p*-methoxyphenylcarbamide), where M= metal ion, i.e. Zn(II), Cd(II) and Hg(II), H_2O-lattice water are present in Zn(II), Cd(II) and Hg(II) polymeric complexes

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