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SYNTHESIS AND OPTICAL PROPERTIES OF METAL FLUORIDE COMPLEXES

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In present work, we have synthesized few metal fluoride complexes (CuF_2, NiF_2, ZnF_2) considering 3-aminomethyal pyridine as ligand. We have investigated their physical properties such as decomposition point, molar conductance, infrared and UV-visible spectra. Molar conductance measurements show that the metal fluorides are electrically active materials and support the electrolytic behavior. The infrared spectroscopic analysis exhibits five major bands that attribute to the octahedral geometry describing the strong correlation between fluorides and metal. Moreover, UV-visible exhibits a strong absorption peaks around 650 nm in both Cu and Ni metal complexes. In addition, we have also estimated the energy band gap from UV-visible spectra and found as 1.45 eV and 1.58 eV for Cu-3-AmP and Ni-3-AmP, respectively. Moreover, the observed energy band gap is inconsistent with the obtained values of conductivity.

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1. Introduction

Chemical compounds which do not give individual ions when dissolve in water are called complex compounds or coordination compounds [1]. The transition metal does have partially filled or empty outer most shells/orbitals which may contribute in the formation of variety of complexes. In most of transition metals, *d* and *f* orbitals are vacant and exhibit some complex formation depending on the electronic configuration. Moreover, ligands have three dimensional structures with metal at the center. However, the complex may be neutral or ionic as can be identified by the total charge of metal and ligands [2].

Prussian blue is considered to be the first known metal complex discovered by Diesbach, a colour maker. However, hexamine cobalt (III) chloride ($CoCl_3.6NH_3$) is also claimed to be discovered in 1798 [3, 4]. In 1861, Herman and Nelson synthesized titanium phenyl-tris (isopropooxide) and organo-tin compound by using phenyl lithium and titanium (IV) chloride. After almost eight years, Bloum and Jorgensen have introduced a "Chain Theory" that defines structures in the form of a series by using cobalt amines of different lengths. In addition, they have also suggested that two valance states may exist for heavy metals. This unique idea of valance bonds have attracted scientists because it helps them to calculate the stoichiometry amount of compounds [5]. Moreover, a detailed "coordination theory" has been introduced by Werner in 1893. However, the best understanding of metal complexes was introduced by Alfred Werner in 1893 and also received a Nobel prize for his theory known as "Werner's Coordination Theory"[6]. Ligands described as the anion or molecules that are bound to metal ions and satisfy the secondary valance condition without being ionized within the solution. The discovery of fluoro complex is named to Helmolt who introduced the fluoro-metellates. Cobalt based fluoride ammonical systems have been investigated by Rahlf and Blitz and reported the successful formation of fluoro

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complexes. Complex or coordination compounds are being used in a huge variety of dimensions and plays a crucial role in many diverse fields such as Biology, Physics, Industry, Agriculture, Medicine and in chemical analysis. Coordination complexes have a key role in the biological system as they naturally exist within the system [7]. Metal complexes have major role in plants. These complexes are light harvesting complexes which are used to capture light and thus help in photosynthesis [8]. Haemocyanin is a Cu based metal complex found in molluscs and crustaceans, used in blood circulations [9]. Hemoerythrin is a red coloured iron containing complex that exists in annelids and used in oxygen transport. Chlorocruorin is agreen coloured iron complex found in annelids [10].

The metal complexes are being used in the formation of electroplating by using the cyanide of complexes. Now a day's metal complexes are also being used in purification of water, preserving vegetables and are also being used as catalysts for polymerization [11]. In light emitting diodes and photovoltaic cells, complexes are used for the conversion of solar energy into electrical energy. Moreover, they can be used as catalysts for transformation of hydrocarbons to other functionalities. C-H bond of hydrocarbons is activated by complexes and temperature is kept lower for reaction conditions [12]. Iron complexes are used for the treatment of hypochromic anaemia as well as ions supplements in body [13]. Platinum complexes are used for treatment of cancers of ovaries, testis and are also used to stop the tumor growth. Moreover, titanium (IV) complexes are used for bacterial oral infections. Cobalt containing complexes are used against the attack of viruses in our body. Iron complexes are used as iron supplements in body (iron-amino acid complex)[14]. Complexes of Zr-89 are used to label antibodies for treatment in tumor therapy [15]. A Fluoro complex consists of metal complex along with the Fluoro ligand inside or outside of the coordination sphere. Nickel was discovered in 1751 by scientists with common oxidation state 2+. Ni (II) can produce variety of stable complexes. The appearance of complexes may be green or blue and their geometry may be octahedral, tetrahedral or square planer depending on the nature of ligands. Cu has various biological applications. Human body contains abundant form of copper in plasma. Zinc form complexes with organic as well as inorganic ligands. Nitrogen and halides form complexes of greater stability with Zn. Most complexes of Zn are diamagnetic in nature. Zn also plays major role in biological system. It is involved in several enzymatic reactions by binding with different enzymes. It is present in liver and muscles in abundant form. It helps in body immunity and preventing several diseases such as cold, fever, and night blindness [27-35]. In this article, we have described the formation of complexes from Ni, Cu and Zn with the combination of 3-Amp as a ligand.

2. Experimental

The entire chemicals Nickel Carbonate (Fisher Scientific), Copper Carbonates (BDH), Zinc Carbonate (Sigma Aldrich), 3-Aminomethyl Pyridine (Merck), Ethyle Acetate (Merck), Methanol (Merck) , Aceton (Merck), Ethanol (Merck), DMF(BDH), CCl4(Merck), DCM (Merck) and HF(Merck). Fluoro complexes of metal (Cu, Ni, and Zn) were synthesized by using the 3-AmP as a ligand. These complexes were prepared by mixing the appropriate amount of metal fluoride and ligand ratio as 1:2. The solvent used for the synthesis of Cu, Ni and Zn complexes were methanol in which 2.5 m mole of copper, Nickel and Zinc respectively about 0.34 g fluoride were dissolved. 3-Aminomethyl pyridine was added to the solvent containing metal fluoride. 5 m mole ligand was added to the solution of metal fluoride (0.5 ml). The solution was then refluxed for 5-6 hours. After this, solution was filtered and filtrate was reduced to a volume of about 10 ml for the growth of crystals. For measurements, we have considered KBr powder and grind it in an agent mortal then we add a small amount of metal fluorid complexes and grind it such that the metal complexes were mixed uniaxial. The obtained grinded powder with mixed metal complex pressed into pellet. For this, we have used Paul-Otto hydraulic manual press under pressure of about 30 KN. The obtained pellet was of the size 13 mm diameters. Moreover, one side of the pellet was made smooth made for spectroscopic measurements. Interaction of ligand with metal occurs through nitrogen present in the structure of ligand. The schematic diagram of such interaction is shown in Fig. 1.

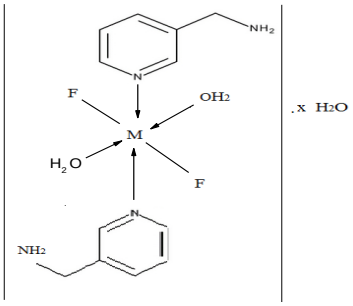

Fig. 1. Structure of metal fluoride complex. Where x may be two or three molecules. Metals are Cu, Ni, and Zn.

3. Results and discussions

The XRD patterns of the sample are recorded on a BRUKER X-ray powder diffractometer using CuKα (1.54060Å) radiation. The scans of the selected diffraction peaks are carried out in the step mode. Synthesized fluoro complexes have different colors. 3-Aminomethyel pyridine (3-AmP) that was used as a ligand has a light yellow coloring liquid form. However, complex of copper synthesized from this ligand was bluish-green in color. Moreover, the Nickel complex was having a light green color. The complex of Zinc was having an off-white color. Interestingly, the complexes of Cu and Ni were crystalline while that of Zn was amorphous. However, all the fluorides of metal under consideration look amorphous, exist in solids state. Although, it is not necessary that all the complexes made from specific ligand must be crystalline. The decomposition temperature of Cu, Ni and Zn were found to be 123 °C, 139 °C and 143 °C respectively. Complexes of Cu, Ni, and Zn were insoluble in methanol and partially soluble in hot water, ethanol, and DMF. These complexes show different behavior from each other in other solvents. The conductance have been measured and found to be 25, 134, 74 μS/cm for Ni, Cu, and Zn complexes.

Infrared (IR) measurements have been performed for ligand and metal fluoride complexes in the frequency range 380-4000 cm^{-1} as shown in Figure 2-5. All the spectra exhibit some absorption peaks that may be described to various modes of vibrations. Coordination between ligand and metal through nitrogen atom can be confirmed through infrared spectra. These spectra are given with detail about different functionalities present in the structure of metal fluoride complexes. The regions in which major peaks are seen have been divided into five parts. Regions are in the range of 3000-3500 cm^{-1}, 1500-2000 cm^{-1}, 1000-1500 cm^{-1}, 600-1000 cm^{-1} and 500-600cm^{-1} respectively. Region I (3000-3500 cm^{-1}) is characterized by the stretching of N-H bond of amino group (NH_2) of complexes as well as ligand, 3-AmP exhibit absorption at a frequency 3020 cm^{-1}. However, the metal fluoride complexes Cu, Ni, and Zn exhibit peaks at 3027, 3021 and 3015, respectively. In region II (1500-2000 cm^{-1}) another band is observed and is attributed to the carbon and nitrogen (-C=N-) bond stretching. 3-AmP exhibits absorption at a frequency 1640 cm^{-1}. However, the metal fluoride complexes Cu, Ni, and Zn exhibit peaks at 1638, 1628 and 1615, respectively. These values of -C=N- stretching are nearly equal to each other and decrease only slightly from Cu to Zn. Region III is characterized by the -C-N- stretching as observed in both ligand and metal fluoride complexes. In case of ligand, this mode is observed at 1422 cm^{-1}. However, in Cu, Ni and Zn complexes these were observed at 1421, 1421 and 1435 cm^{-1}, respectively. The interaction of metal and ligand determines how these values may differ from each other.

Table 1. Comparison of major IR bands of 3-AmP and their metal complexes.

Description	3000-3500 (cm^{-1})	1500-2000 (cm^{-1})	1000-1500 (cm^{-1})	600-1000 (cm^{-1})	500-600 (cm^{-1})
3-AmP	3020	1640	1422	707	----
Cu-3-AmP	3027	1638	1421	705	552
Ni-3-AmP	3021	1628	1421	708	543
Zn-3-AmP	3015	1615	1435	706	570
Band Assignment	-O-H- -N-H- Stretching	-C=N- Stretching	-C-N- Stretching	Ar-H Bending	M-N M-F Stretching

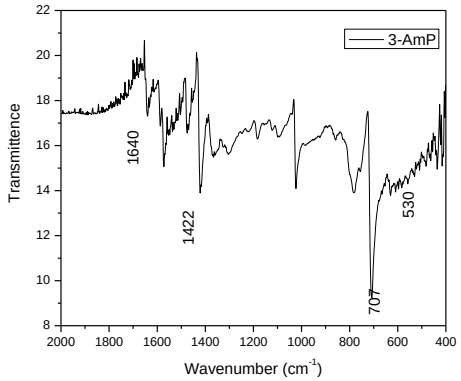

Fig. 2. Fourier Transform infrared spectroscopy of 3-Aminomethyl Pyridine (3AmP).

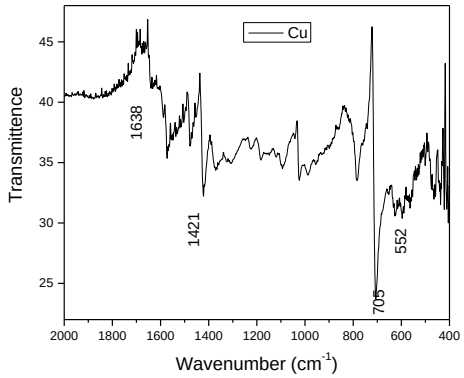

Fig. 3. Fourier Transform infrared spectroscopy of Cu-3AmP.

Region IV (600-1000 cm^{-1}) is the most important and prominent region representing the major band that may be attributed to the aromatic bending (Ar-H). Interestingly, all the bands observed in this region are much close to each other and show no obvious change due to addition of ligand and change in metal fluoride. In case of ligand, this mode is observed at 707 cm^{-1}. However, in Cu, Ni and Zn complexes these were observed at 705, 708 and 706 cm^{-1}, respectively. Finally, the last region V is related to the absorption pattern of metal, nitrogen, and metal fluorine that corresponds to M-N and M-F stretching. In this region, there exists M-F vibrations that show higher wave numbers greater than M-N frequencies. It is due to the fact of electronegative nature of fluorine. In this region, corresponding frequencies of Cu, Ni, and Zn are 552, 543, 570 cm^{-1}, respectively. The peak value increases as we move from Cu to Zn, which is in contrast

to region-II. 3-AmP contains six members of aromatic rings. It behaves as momodentate ligand and coordination of metal is observed through nitrogen of pyridine. Preparation of complexes is accomplished in solvent which are either water or alcohol. Due to these solvents, molecules of H_2O are involved in coordination with metal which is involved in complex formation.

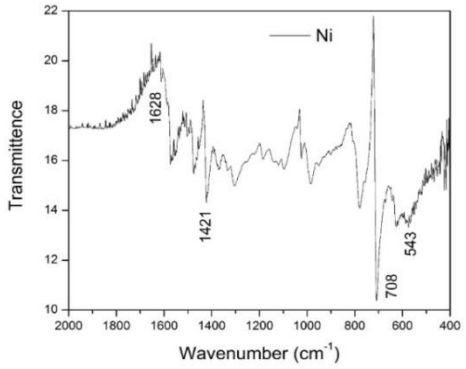

Fig. 4. Fourier transform infrared spectroscopy of Ni-3AmP.

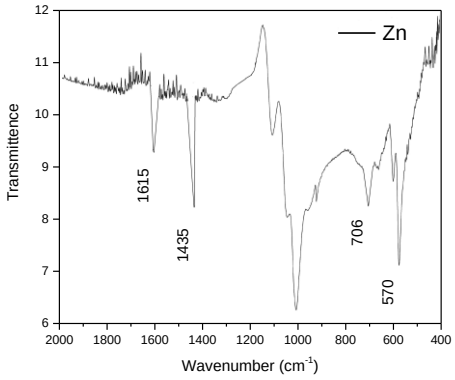

Fig. 5. Fourier transform infrared spectroscopy of Zn-3AmP.

The UV-visible absorption spectra of Cu and Ni complexes have been measured by using Dynamic HALO, DB 20, UV-vis double beam spectrophotometer. Fig. 6 demonstrate the UV-visible spectrum of Cu-3AmP metal fluoride complex in the wavelength range 450-900 nm. There is a strong absorption edge around 650 nm and a cut-off absorption is observed at 900 nm indicating that the material can absorb light in most of the visible spectra (390-780 nm). The energy band gap (Eg) can be obtained by extrapolation of the rising part to the plot to the wavelength axis [36, 37]. We have estimated the absorption edge value around 880 nm, which gives an energy band gap of about Eg = 1.40 eV. Fig. 7 exhibit the UV-visible spectrum of Ni-3AmP metal fluoride complex in the wavelength range 450-900 nm. There is a strong absorption edge around 650 nm and a cut-off absorption is observed at 850 nm indicating that the material can absorb light most of the visible spectra (390-780 nm). We have estimated the absorption edge value around 780 nm, which gives an energy band gap of about Eg = 1.58 eV. The obtained values of energy band gap is consistent with molar conductance. Moreover, the energy band values exhibits the semiconducting nature of the complexes.

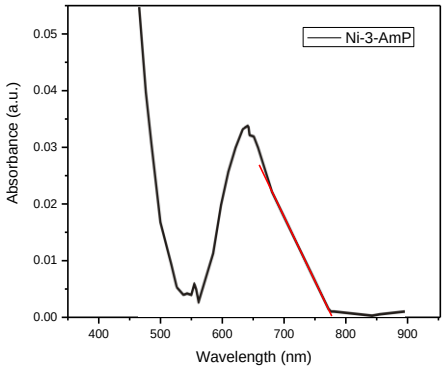

Fig. 6. UV visible absorption spectroscopy of Ni-3AmP.

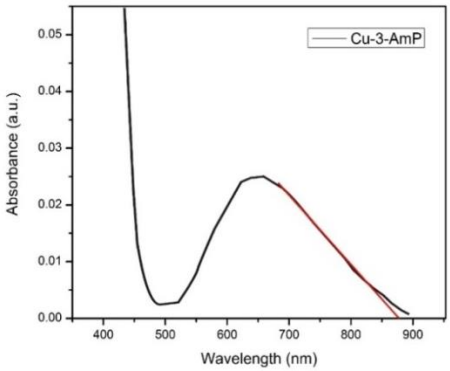

Fig. 7. UV-visible absorption spectrum of Cu-3AmP.

4. Conclusions

In present work, we have successfully synthesized metal fluoride complexes (CuF_2, NiF_2, ZnF_2) with coordination of 3-aminomethyal pyridine as ligand. The prepared samples have been characterized by using decomposition point, molar conductance, infrared and UV-visible spectroscopy. The infrared spectroscopic analysis exhibits five major bands for metal fluoride complexes and only four bands in the ligand spectrum. The extra band that is only observed in metal fluoride complexes are attributed to the M-N / M-F stretching.

A small deviation in the band frequency has been observed in all metal complexes as compared to that of ligand indicating the proper formation and structural of metal complexes. Ni-3-AmP has found to be less conducting material with energy band gap of about 1.56 eV at room temperature. In contrast, Cu-3-AmP has maximum conductance while exhibiting energy band gap of about 1.45 eV. The obtained values of molar conductance and optical energy band gap indicating the semiconducting behavior of metal fluoride complexes. The obtained results are very much encouraging and would be of great interest for the scientific community in order to gain better understanding about fluorides and their possible applications in biomedical and future technology.

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