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Synthesis and Characterization of Coordination polymers of Bis-(mercaptoacatamido)–Butanedioane Dihydrazone

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Abstract: ***Coordination polymers of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd (II) with bis-bidentate ligand delivered from mercaptoacetic acid and 2,3 butanedione dihydrazone have been prepared. All polychelates are coloured, amorphous solid insoluble in water and common organic solvents and characterized with the aid of analytical, magnetic, spectral and thermal studies. The Mn(II),Co(II) and Ni(II) polychelates are of a six co-ordinated octahedral structure, where as Zn(II) and Cd(II) polychelates are found to be four co-ordinated while Cu(II) exhibit square planer structure respectively. Elemental analysis indicators a metal: ligand ratio 1:1 by using graphical Freeman–Carrol method various thermodynamics parameters have also been evaluated. Thermal stability of the complexes have been tested for their antibacterial activity against the bacteria E coli, Bacillus sp, stappylocous and Pseudomonus sp. The solid state conductivity of ligand and complexes were also measured in their compressed pettet from in the temperature range 310-450 K and all complexes were are found to be semiconducting in behaviour.***

Keyword: Coordination polymers, magnetic studies, spectral studies, TG /kinetic, parameters /electrical conductivity and biological activity

1. Introduction

In recent years there are been a considerable interest in the polymer metal complexes due to their practical convenience and operational flexibility.The first row transition metals are characterized by their ability to form a wide range of coordination complexes in which the octahedral,tetrahedral and square planer stereochemistry predominate,while inspired us to prepare bis-bidentate ligand which would be able to form complexes with variety of transition metals[1]. This paper describes the preparation and characterization of the polychelates prepared from bis-(mercaptoacetaletamido) but anedione dihydrazone (BMABD)[2].The stereochemistry of the polychelates have been studied from the diffuse reflectance spectra infrared spectra, magnetic moment and thermal analysis D.C. Electrical conductivities and biological have been measured in pellet form.

2. Material and Method

All the chemical used were of chemically pure quality and solvents were used after double distillation.

Synthesis of bis-(mercaptoacetaletamido)-butanedione dihydrozone (BMABD):2,3 butanedione dihydrazone was prepared by known method [1]

To a hot solution of mercaptoacetic acid (0.2m) in 20ml methanol in 500ml round bottom flask, few drops of conc. H_2SO_4 were added and mixture was refluxed on water bath for about 45min and then as solution of 2,2- butanedione dihydrazone (0.1) in 20ml methanol was added in the same flask with constant stirring and reactions mixture was refluxed for another 30min. and left to cool,where upon the yellow crystal which had formed were filtered off and washed several times with water, methanol and ethanol to unreacted reactant product was crystallized from DMF :yield 71% , M.P.218^{0}C.

Synthesis of coordination polymers: All the coordination polymers isolated in the present study were prepared by the following general method.

Metal acetates [chloride in case of Cd(II)]and ligand BMABD were dissolved in minimum quantity (20-40ml) of DMF separately in molar ratio 1:1 Both the solutions were filtered and mixture in hot condition with constant stirring. Then the reaction mixture was refluxed on oil bath for 5h. The coloured products obtained with different metals were filters, washed thoroughly first with DMF then with absolute ethanol followed by acetone and dried in vacuum desiccators over calcium chloride.

Physical Measurements:

The C, H and N contents were analysed on contents analysed on Coleman's Analyser. The metal content in each polychelates was determined by classical oxide method [2].The magnetic susceptibitilities were determined at room temperature by Gouy's method using $Hg[Co(NCS)_4]$ as celebrant and experimental magnetic susceptibilities values were corrected diamagnetism The diffuse reflectance measurements were made on Karl-Zeiss VSU-2P spectrometer using MgO as celebrant.The IR spectra were recorded on a Perkin –Elmer (model-577) spectrometer . Thermogravimetric analysis was carried out on a Perkin Elmer TG system TGS-2 at a heating rate of 10^{0}C per unit in air atmosphere.D.C.electrical conductivities were measured by voltage drop method using D.C. microvoltage meter in pellet form.

3. Results and Discussion

All The coordination polymers are coloured amorphous solid and were found insoluble in water and common organic solvents. The elemental analysis dada of the polychelates corresponds to the general formula ML or (ML)n (Table 1).

Infrared Spectra:

The IR spectra provide important ion the coordination sites of metal ions to the ligand. Comparison of IR spectra of the chelates and ligand reveal that the spectra of polymeric chelates do not significantly differ from each other but they do differ from that of ligand in certain. The IR spectrum of the ligand displays three medium intense medium intense bands at 3320,1560 and 930cm^{-1}which can be assigned to–NH,-C=N and N-N- stretch respectively[3-4].These bands are shifted to a lower frequency region by 20-30cm^{-1} in spectra of polychelates suggesting coordination of the metal ions through nitrogen of the NH group. A sharp band at 2600cm^{-1} in the spectrum of ligand is a characteristic of SH stretch. This band disappears in all the coordination polymers which indicate complexation by replacing proton from –SH group. The ligand spectrum shows one medium band at 1480 cm^{-1}due to S-CH_2 group. This has been found at lower (10-20 cm^{-1}) frequency in the chelates indicating formation of metal-sulphur bond by removing proton of –SH group. A band at 1660cm^{-1} (C=O) in the ligand remained unreacted in all chelates suggesting the absence of coordination through oxygen (C=O) Appearance of new bands in the chelates polymers in the region 410-560 and 340-360cm^{-1} suggests M-N and M-S bonding respectively. Mn(II) ,Co(II) and Ni(II) polychelates display abroad band in the range 3400-3500cm^{-}1 [5]which may be attributed (OH) to water these polychelates also exhibit weak bands around 1575 and 780cm^{-1} which are assigned to coordinated water suggesting six coordinated structure.[6] This is further confirmed by TG analysis.

The magnetic moment and reflectance spectral data of coordination polymers are shown in table1.The magnetic moment of Mn(II) polychelates is 5.41B.M. suggesting there by octahedral geometry. The reflectance spectrum of Mn(II) Chelates shows low intensities of the bands as a consequence of their doubly forbidden nature in normally expected regions for octahedral structure. The Co(II) chelate has a magnetic motet 4.78B.M. [7-8]which is in good agreement with high spin octahedral geometry, since spin only value for three unpaired electronic spectrum of Cu(II) polychelate shows three bands around 15705,12363 and 10638 cm^{-1} in their normally expected region for square planar Cu(II) complexes. The broadness of these bands any be indication towards lower symmetry. The magnetic moment of Cu(II) chelate is 2.01B.M.indicative of the from square planar geometry. The polychelates of Zn(II) and Cd(II) are found to be diamagnetic as expected for d^{10}system and four coordinated tetrahedral geometries have been suggested basing upon analytical and IR spectral data.

The possibility of water molecules, suggested and IR spectrum,is confirmed by TG analysis. In the present study, weight losses of Mn(II),Co(II) and Ni(II) polychelates at around 1060-220^{0}C are 9.46 ,10.46 and 10.30% respectively. These weight losses corresponds to two coordinated water molecules per repeating unit of polychelates. The Cu(II),Zn(II) and Cd(II) polychelates lost water loss water around 130^{0}C[9] which are probably crystal water. The observed weight loss is a little higher than required in these regions and this may be due to some other chain degradation reaction involved in pyrolysis of chelates. The procedural decomposition temperature for the polychelates decrease the order Co>Ni> Mn> Zn> Cu . In some case decomposition occurred at a lower temperature which may be due to oxidation of the polymer by the catalytic action of these metal ions.[10-11].The analysis of the thermogram indicates that the polychelate decompose in two stages after the loss of the water molecules and decomposition in first step is rapid as compared to the second step. The decomposition is complete at about 700^{0}C leading to the formation of stable oxides. For calculation of activation energy of thermal decomposition, the Sharp-Wentworth [12] and Freeman–Carroll [13] methods were used and comparable values are cited in table 1. By using graphical data of Freeman–Carroll method various kinetic and thermodynamic parameters have also been evaluated and summarized in Table 1. Their values are all very similar, which indicate a common reaction mode. The abnormally low values of Z indicate that the decomposition reaction of the polychelates can be classed as a slow reaction. The values of ΔS for the polychelates are negative which indicate that the activated complex has a more ordered structure than reactants and than the reactions are slower than normal.

The electric conductivity of the ligand and its polychelates were studied over a wide range of temperature (303-540K). According to the solid state theory, the plots of logarithm conductivity *vs* the reciprocal of absolute temperature should yield straight line over given temperature ranges according to relation $\sigma = \sigma^0 \exp(E_a/KT)$, where σ^0 is a constant, E_a is the activation energy of electrical conduction, T is the absolute temperature and K is Boltzman constant[14-15].The activation energy decrease in the order BMABD Zn>Ni>Co>Cd>Cu>Mn which is in partial agreement with reported results. It seems from the data that it is lone pair of electrons of nitrogen atom which is most affected by complexation, removal or binding which decrease the conductivity.

Antimicrobial activities of the ligands and the complexes have been carried out, against the bacteria *E coli,Bacillius sp.,Staphylocous and Pseudomonous sp*. using nutrient agar medium by the disc diffusion method. The test solution were prepared in DMSO to a final concentration of 0.01% and 0.02% and soaked in filter paper of 5mm diameter and 1 mm thickness. There disc were placed on the already seeded plates and incubated at 35^{0}C for 24 hours. The diameter (mm) of the inhibition zone around each disc was measured after 24 hours and results are listed (Table-2) Streptomycin was used as standard. It was been observed from these studies that the metal complexes have a higher activity than the free ligands against the same microorganism under the identical experimental conditions. The mode of action of the complexes may involve the formation of hydrogen bonds involving the azomethine group with microbial or ribosomes of microbial cells resulting in interference with normal cell processes. The toxicity increase with increasing concentration of the complexes. [16-19].

4. Conclusion

Here we have reported preparative and structural studies of metal coordination polymers of bis-ligand. All coordination polymers are insoluble in common organic solvents. It was not possible to characterize them by conventional methods, like osmometry, viscometry, conductometry, etc., as they are insoluble. The nature of ligand, high thermal stability, metal-ligand ratio (1:1) and insolubility of these compounds suggest their polymeric nature. The Mn(II),Co(II) and Ni(II) polychelates are of a six co-ordinated octahedral structure .where as Zn(II) and Cd(II) polychelates are found to be four co-ordinated while Cu(II) exhibit square planer structure respectively.

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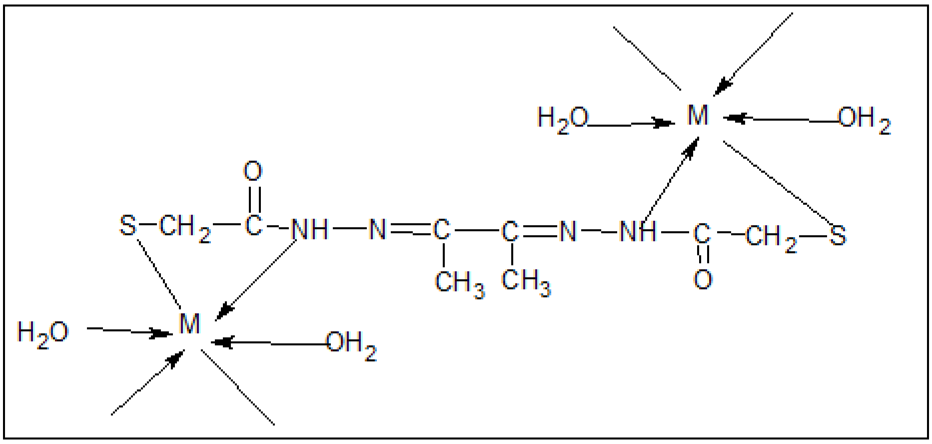

Mn(II),Co(II),Ni(II),Cu(II) ,Zn(II) and Cd (II)
For Cu(II) ,Zn(II) and Cd(II) coordinated H_2O molecules absent

Table 1: Thermal and Electrical conductivity data of Coordination Polymers

Ligand	Electrical DecompositionTemp	Activation Energy (eV)	DH (^{0}C)	Method	E (Kj mol^{-1})	ΔH (S^{-1})	ΔS(JK^{-1}mol^{-1})
BMABD	$9.70\text{x}10^{-12}$.	0.31	355	F-C	29.49	90.44	-281.40
				S-W	27.95	160.40	-280.15
BMABD -Mn	$5.811 \text{ x } 10^{-8}$	0.190	390	F-C	24.14	204.57	-208.4
	$3.723 \text{ x } 11^{-8}$			S-W	28.09	375.81	-240.20
BMABD -Co	$3.126 \text{ x } 10^{-9}$	0.245	340	F-C	25.40	153.08	-280.67
	$1.010 \text{ x } 10^{-8}$			S-W	29.23	270.45	-280.54
BMABD -Ni	$2.392 \text{ x } 10^{-6}$	0.583	250	F-C	21.06	320.59	-273.38
	$7.735 \text{ x } 10^{-6}$			S-W	24.75	220.17	-281.42
BMABD -Cu	$6.001 \text{ x } 10^{-6}$	0.863	310	F-C	16.14	330.05	-280.14
	$9.410 \text{ x } 10^{-6}$			S-W	18.90	320.92	-276.48
BMABD -Zn	$1.362 \text{ x } 10^{-8}$	0.749	320	F-C	20.61	148.51	-264.27
	$2.023 \text{ x } 10^{-8}$			S-W	19.14	160.58	-258.91
BMABD -Cd	$1.699 \text{ x } 10^{-8}$	0.238	305	F-C	18.94	84.28	-210.45
	$4.948 \text{ x } 10^{-7}$			S-W	20.40	136.35	-215.28

F-C = Freeman-Carroll, S-W = Sharp-Wentworth and DH - Half Decomposition temp.

Table 2: Antimicrobial data of ligand and their complexes

Compound	*E coli* (mm)	*Bacillius* sp (mm)	*Pseudomonous* sp.(mm)	*Staphylocous* (mm)
BMABD	6.8	5.6	6.7	6.9
BMABD- Mn	9.12	8.10	9.11	9.10
BMABD -Co	10.11	10.13	12.13	10.12
BMABD -Fe	9.11	8.12	9.12	11.12
BMABD- Ni	8.10	6.7	6.9	7.9
BMABD -Cu	9.12	10.11	12.14	10.11
BMABD -Zn	11.14	10.14	11.19	10.12
BMABD -Cd	10.12	12.14	12.13	10.13
Streptomycin	18.21	20.23	18.21	18.22