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THERMAL AND ANTIMICROBIAL STUDIES OF SOME BENZILIC ACID - AMINO ACID TRANSITION METAL COMPLEXES

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ABSTRACT

Anti microbial agents are used to prevent diseases of plants and animals. Synthesis of a new series of Cu, Ni, Mn, Co complex of benzilic acid-amino acid have been carried out and its characterization were fulfilled by various physicochemical methods such as elemental analysis, molar conductance and UV and IR spectral measurements. Magnetic and conductance data of these complexes have also been employed to characterize them. Thermally stable coloured complexes of amino acid alanine with benzilic acid and metals were prepared and their antifungal activity tried against Rhizoctonia solani, Phytophthora capsici and Colletotrichum gloeosporioides. The novel thermally stable bezilic acid alanine complexes synthesized show high antifungal activity.

KEYWORDS: Benzilic acid, Alanine, Rhizoctonia solani, Phytophthora capsici, Colletotrichum gloeosporioides. Anti fungal activity.

INTRODUCTION

The use of Amino acid transition metal complexes as antimicrobial agents has been reported recently. During the past decades, much importance has been given to the synthesis of new transition metal complexes and the evaluation of these agents for their antibacterial and antifungal activity. In the last few years so many studies has been done on the structure and chemical behavior of several metal complexes to find out an alternative against the antimicrobial drugs. This study emphasis special interest to the discovery of the new metal complexes possesses antibacterial and antifungal activity. A survey of literature has indicated that no work has been done on Cu (II), Ni (II), Mn (II) and Co (II) complexes of benzilic acid and amino acid hence the same was undertaken and findings are reported in the present paper. The physicochemical investigation on the bivalent metal complexes was carried out by conductometric, magnetic and spectral techniques with the object to compare their properties. Alanine is an alpha-amino acid encoded by the genetic code. It occurs in bacterial cell walls and in some peptide antibiotics and is an intermediate in sugar metabolism, cause higher blood pressure in human when present in large quantity. Rhizoctonia solani is a soil born plant pathogen cause plant diseases like collar rot. Phytophthora capsici is a plant pathogen that causes foot rot of peppers and Colletotrichum gloeosporioides is a fungus which attacks fruits, ornamental plants etc.

Stanila and Braicu.[1] from Romania studied the antibacterial activity of copper and cobalt amino acid complexes using ligand methionine, phenylalanine, valine, leucine, lysine and tested their antimicrobial efficiency on Esherichia coli, basiluscerus, micrococus latecus. A S K Kuwar et al [2] studied the synthesis, characterization and microbial activities of octahedral transition metal complexes of Ni, Cu and Zn. The thermal stabilities of metal chelates with azomethine group was studied by Aravindakshan and Muraleedharan.[3] Muhammed et al.[4] have reported Synthesis and characterization of new metal complexes of valine. Subhasish Saha, et al.[5] studied the synthesis, characterization and antimicrobial activity of cobalt metal complex against multi drug resistant bacterial and fungal pathogens. In Vitro anti microbial activity of new organo tin (IV) complexes of Schiffbases derived from amino acids have been reported by Nath mala and Yadav Rakesh.[6] In this study emphasis is given to the development of thermally stable modern effective fungicides derived from benzilic acid –alanine and alanine complexes of Co (II), Mn (II), Ni (II) and Cu (II).

EXPERIMENTAL

All chemicals (purity from 98-99%) were purchased and used without further purification. Chemicals used were analar Grade Benzilic aicid-amino acid ligand were prepared using the reaction between Benzilic acid with

amino acids. All the four complexes were synthesized by mixing aqueous methanolic solution of metal acetate with the aqueous methanolic solution of Benzilic acid-amino acid. The complexes were filtered, washed and dried. Standard methods like volumetric, gravimetric or pyrolytic techniques were adopted for the estimation of metal content in the complexes. Conductivity of complex was determined using conductivity cell, melting point of the ligand and complex determined by melting point apparatus. IR spectra were recorded on a Jasco mode FT-IR spectrophotometer. UV spectrum and magnetic moment measurements were carried out.

Antifungal Activity

Benzilic acid-alanine complexes of copper, cobalt, nickel and manganese were subjected to antifungal studies by agar plate technique against viz. Rhizoctonia solani, collectotrichum and phytophthora capsici at different concentrations. Plates incubated at room temperature and observations were recorded after 24, 48, and 72 hours.

Thermal Study

Thermal studies of these complexes were carried out on the basis of Mechanic and Non Mechanistic equations. Thermogravimetric analysis of these coordination compounds were made in static air atmosphere at a heating rate of 10ºC/minute ,by using about 2-5 mg of the sample.

RESULTS AND DISCUSSION

The metal percentage of the complexes have been obtained from the analytical data summarized in Table.1. All the complexes possess molar conductance in the range below $15\Omega^{-1}$ cm^2 mol^{-1} in agreement with their non-electrolytic nature. Determination of coordination of ligands is observed from the infrared spectra.

Characterization of Ligand and complex: Melting point of Benzilic acid alanine measured as 168^0C. The metal to ligand ratio in alanine - benzilic acid metal complexes was 1:1. All the complexes possess molar conductance in the range below 15 cm^2 mol^{-1} -1 cm^2 mol^{-1}. Melting point of various complexes ranges from 212^0C to 240^0C and for the ligand it is only 168^0 C.

Table 1: Benzilic acid Alanine complexes (L = Benzilic acid Alanine).

Metal Complex	Color	Melting point	M%	Ω^{-1}
$CuL(H_2O)$	white	225	16.78 (16.53)	9.1
$CoL(H_2O)_4$	pink	232	13.77 (13.51)	14.8
Mn L $(H_2O)_2$ CH3COO	white	240	12.29 (12.42)	.9
$NiL(H_2O)_2$	Bluish green	212	14.98 (14.9)	7.4

New bands are found in the spectra of the complexes in the regions 444–537 cm^{-1}, which are assigned to (M–O) stretching vibrations. In the IR spectra peaks at 3700-3200cm^{-1} is used to locate the following bonds: the alcohol O-H, the terminal alkyne C-H and the amine and amide N-H. In complexes, the alcohol peak at 3618-3568cm^{-1} shows that OH group involved in coordination. The SP^3 C-H bond peaks appeared at 2899-3031cm^{-1} in complexes and ligands. The SP^2 C-H bonds can be distinguished because they are located slightly to the right of the 3000cm^{-1}. Peaks at1600 cm^{-1}, 1560cm^{-1}, 1493 cm^{-1} show the presence of benzene ring in ligand and complexes. Rings almost show a weaker sharp peak right at 1600 cm^{-1}.The (OH),(C=O),$_{asym}$(coo) and $_{sym}$(coo) stretching vibrations are observed at 3398cm^{-1}-3400cm^{-1},1631,1594 and 1337cm^{-1}. The participation of the carboxylate-O atom in the complexes formation was evidenced from the shift in position of these bands to 3248-3332,1621-1747,1493-1619,1395-1455cm^{-1} in metal complexes. New bands at regions 449-531cm^{-1} assigned to (M-O) stretching vibrations. The bands at 470-502 cm^{-1} have been assigned to (M-N) mode. The IR spectra of cobalt, nickel and manganese complexes showed a broad band at 3400cm^{-1} that can be assigned to the va(OH) and va(SH) vibration modes from water molecules. The IR spectrum at 3031 and 3065cm^{-1} is due to the asymmetric and symmetric vibrational frequencies of NH amide group and a band at 1495cm^{-1} was assigned to (N-H) of amide. In most of these complexes, band at the same position confirming that the nitrogen atom of the NH moiety does not participate in the coordination in Ni, Co, and Cu complexes. The spectra of the copper chelates displayed two new bands in the range of 417-476and 476-531 cm^{-1} which were assigned to γ M-O and γ M-N respectively. The IR spectra Manganese complexes showed a broad band at 3400 cm–1 that can be assigned to the va(OH) and vs(OH) vibration modes from water molecules. The electronic spectrum of Cu(II) complex also shows a broad band in the region 410-700 nm (38461-16949 cm-1) is assignable to d-d transition .In d7 cobalt complex it show three absorptions. Two bands have been found at 220 nm and 270 nm in case of free ligand. The electronic spectra of metal complexes different from that of the free ligand indicating that the ligand has changed its structure in the complex. The band at 220 nm in the spectra of the complex is shifted compared to the free ligand suggesting carboxylic group participate in the complex formation. The three absorption bands observed at 220 nm, 265 nm, and 540 nm. i.e electronic spectra of Mn(II) complex exhibited a band at 22727 cm^{-1} which was taken as evidence to support octahedral geometry. The cobalt complex shows

two bands, a broad and weak band at 14285 cm-1 assigned to 4T1g →4T2g and a weak shoulder at 12345cm-1 for 4T1g →4T2g (P). These complexes possess octahedral geometry

Antifungal Activity

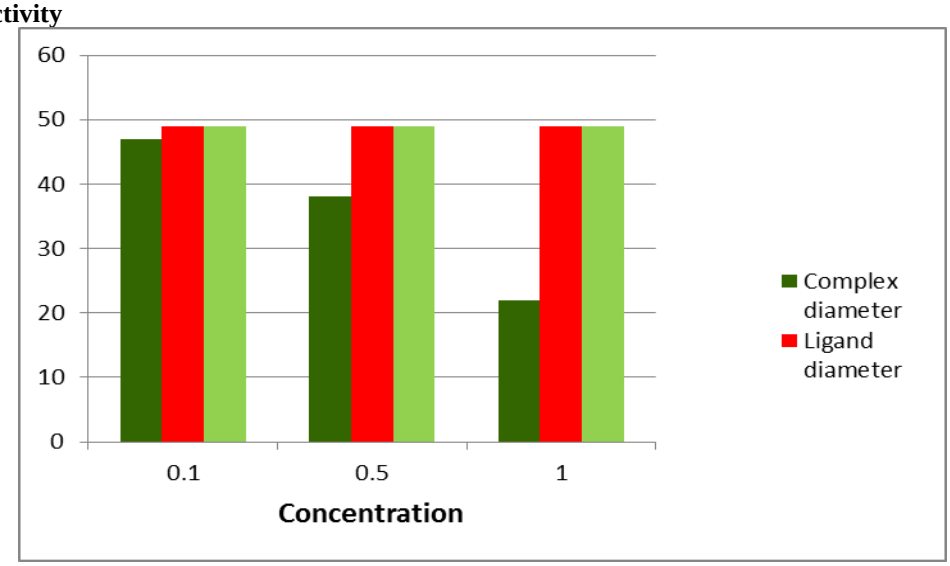

Figure 1: Rhizoctonia Solani Co Complex – 72 hours.

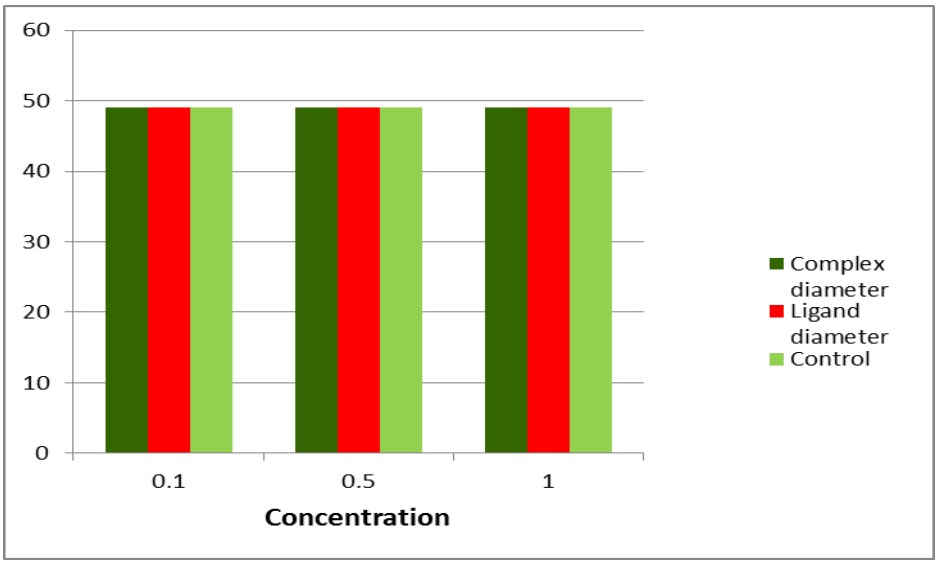

Figure 2: Rhizoctonia Solani Cu Complex – 72 hours.

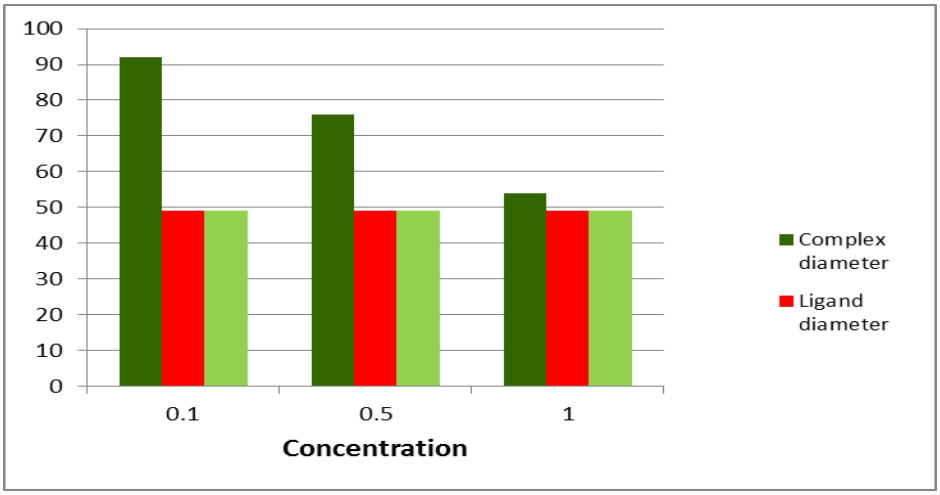

Figure 3: Phytophthora Capsici Co Complex – 72 hours.

The data indicates that lower concentration of copper and cobalt complexes possess same percentage inhibition on mycelia growth and from the results it was found that manganese and cobalt complexes do not show any inhibition in both fungi. The % inhibition plots of various compounds are given below.

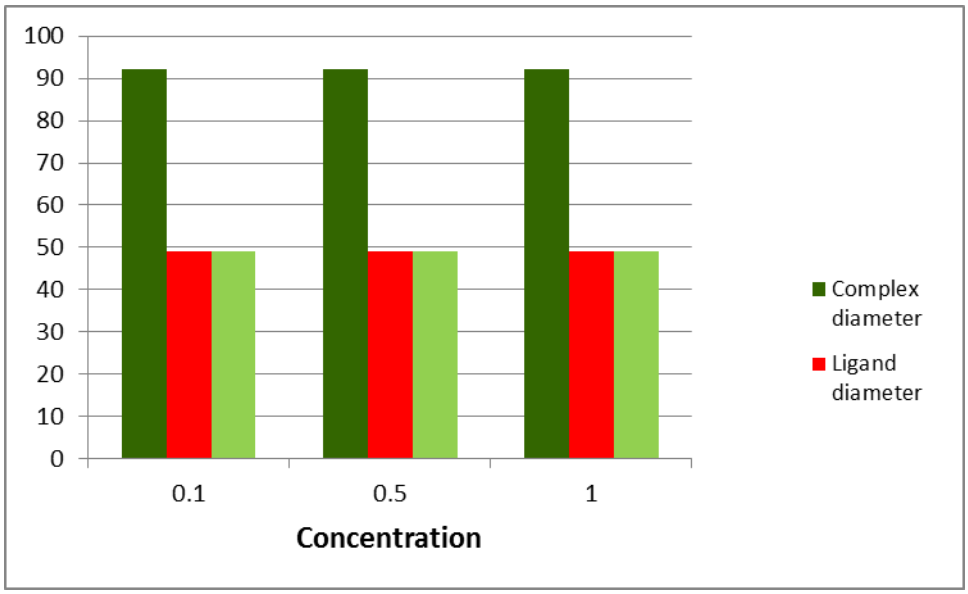

Figure 4: Phytophthora Capsici Cu Complex – 72 hours.

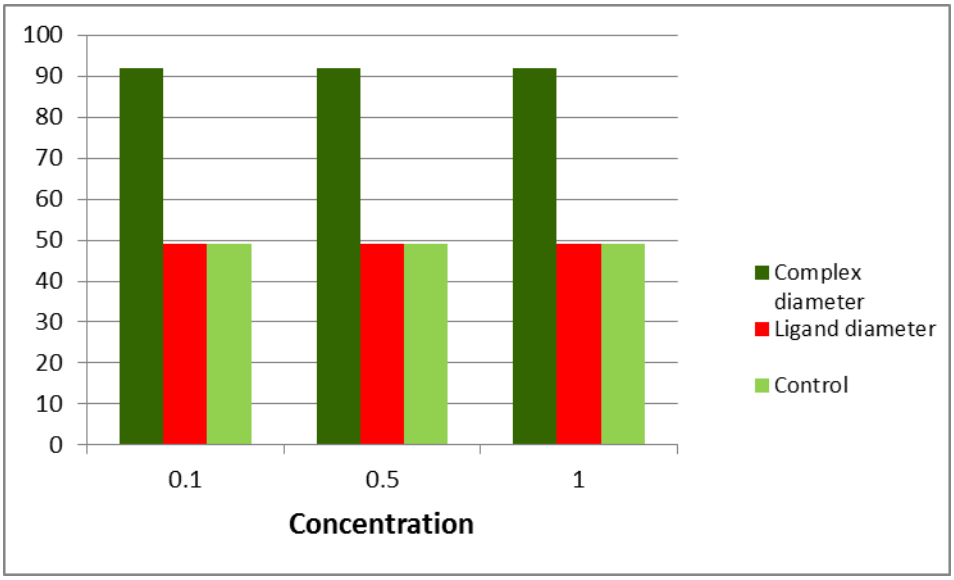

Figure 5: Phytophthora Capsici Mn Complex – 72 hours.

Above graphs were plotted between mycelia growth measured in diameter and concentration. Results shows that both the ligand and complexes possess moderate inhibition on phytophthora capsici and Rhizoctonia solani on its mycelia growth phase in the higher concentration. Copper and cobalt complexes possess almost same percentage inhibition. Cobalt complexes shows poor inhibitory rate in both fungi. Result shows that it can be effective at very high concentrations. For cobalt and Manganese complexes, ligand and control shows same rate of mycelia growth. From this it was found that manganese complexes and cobalt complexes does not show any inhibition in both fungi.

Thermal Studies

Various kinetic methods, both mechanistic and non-mechanistic equations (Coats Redfern and Horowitz-Metziger equations) have been utilized in order to analyze the decomposition curve. All the TG curves were subjected to kinetic analysis and kinetic parameters namely, energy of activation, Arrhenius frequency factor and entropy of activation of decomposition have been calculated. All the complexes were thermally stable.

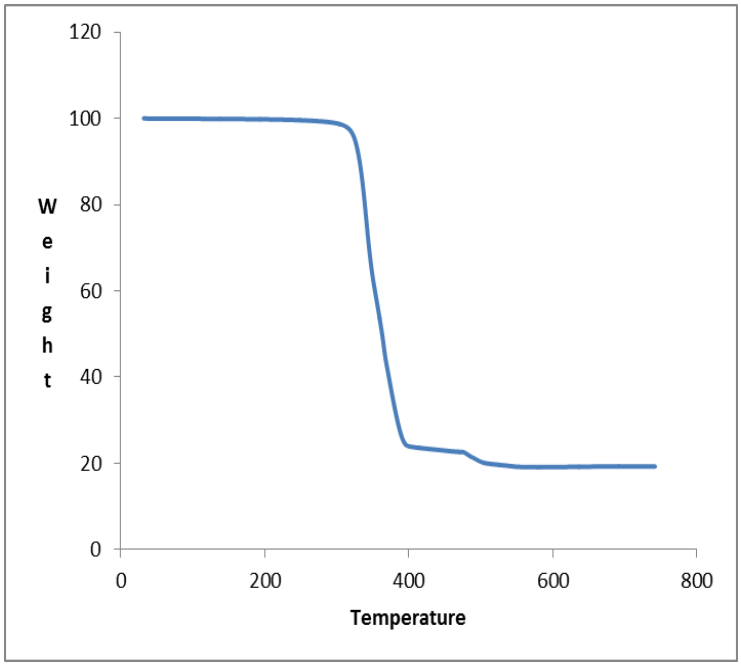

Figure 6: TG curve of Co Benzilic acid alanine complex.

These complexes show detectable change up to 100^0C when heated, which suggest that there is water of hydration. At around 200 ^{0} C, a loss of mass is noted in the case of Co (II), Ni (II), Mn (II)and Cu (II) complexes which can be attributed to the loss of coordinated water molecules. Co (II) complexes having the formula [Co L $(H_2\ O)_4$], exhibit two stage decomposition pattern, one stage can be assigned to the loss of molecules of water and the other due to the loss of ligand part. The Ni (II) complex having the formula [Ni L $(H_2\ O)_2$] also exhibits a double stage pattern of decomposition. The first stage shows the loss of one-coordinated water molecule. The second stage in the TG curve shows the removal of benzilic acid -alanine part.

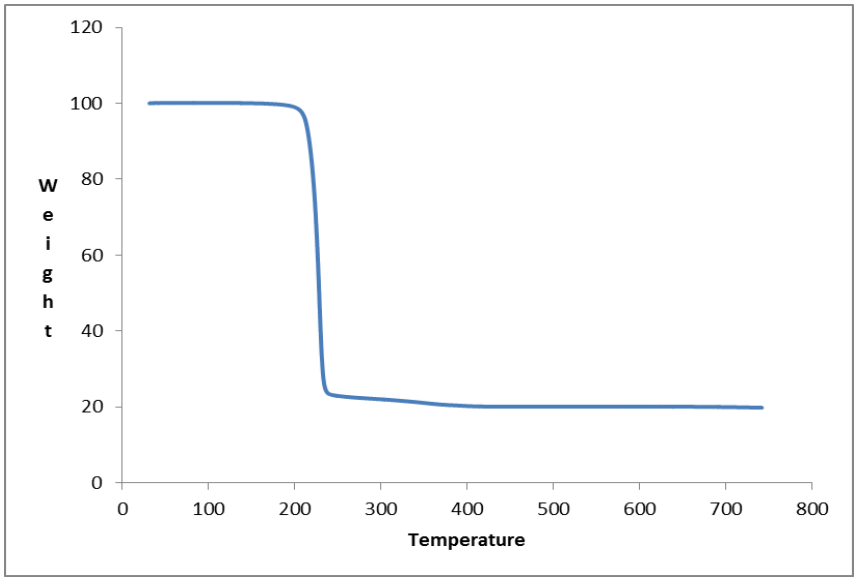

Figure 7: TG curve of Cu Benzilic acid alanine complex.

The TG curve of the Cu (II) complex exhibits a clear well defined two stage decomposition patterns. The first stage may be attributed to the loss of one molecule of water and the second stage contributes to the loss of ligand. In Mn (II) complex first stage attribute the removal of one molecule of water and second stage involve the removal of one water molecule, ligand and acetate part. The final mass loss observed agrees with the values calculated for the conversion of complexes to their oxides. The initial decomposition temperature is frequently used to define the thermal stability of metal chelates. Based on experimental results the relative thermal stability of these chelates can be given as [Co L $(H_2O)4$] >[Cu L (H_2O)] > MnL $(H_2O)2$ (CH3COO) > [Ni L $(H_2O)_2$]

The values of kinetic parameters obtained using the various non-mechanistic equations and the equation corresponding to the suggested mechanism of decomposition, are reasonable and are in good agreement. The satisfactory value of correlation coefficient, ($r \approx 1$), indicates good agreement with experimental data. The negative ΔS values of these complexes show that the complexes are more ordered in the activated state than the reactants and the reactions are slower than normal.

The order parameter n, and the kinetic parameters such as activation energy E, pre exponential factor A and entropy of activation ΔS for the thermal decomposition of these four complexes were evaluated. It is also found that the greater the thermal stability of the complex, the larger the activation energy for decomposition. In the present course of studies based on these mathematical evaluations, it is observed that the kinetic parameters calculated for the decomposition of Co (II) complex from the Coats Redfern equation with n =2/3 is in good agreement with those obtained for the R3 mechanism. R3 mechanism based on phase boundary reaction Spherical symmetry gives maximum correlation for [Co L $(H_2O)_4$] and for CuL (H_2O) .

For the decomposition of Ni (II) complex and Mn (II) compllexes, kinetic parameters obtained from Coats Redfern equation with n = 1/2 are in good agreement with those obtained for the R2 mechanism based on phase boundary reaction cylinderica symmetry. Thermal stability of these chelates can again confirmed as [Co L $(H_2O)_4$] >[Cu L (H_2O)] > MnL $(H_2O)2$ (CH3COO) > [Ni L $(H_2O)_2$]. All these eight complexes were thermally stable.

CONCLUSION

In this study, emphasis is given to the development of new thermally stable transition metal complexes of benzilic acid amino acid metal complexes, and to study its impact on various diseases developed by fungus in plants. Ligands and complexes were synthesized and their structural elucidation based on elemental, electrical, magnetic, spectral and thermo gravimetric methods were carried out. Formulas of benzilic acid – alanine complexes were assigned are [Co L $(H_2O)_4$] >[Cu L (H_2O)] > MnL $(H_2O)2$ (CH3COO) > [Ni L $(H_2O)_2$]. L is the ligand benzilic acid – alanine

For Antifungal studies healthy culture of Rhizoctonia solani, colletotrichum, and phytophthora capsici were used. Antifungal studies reveal that cobalt complexes were moderate inhibitors. Manganese and copper complexes does not have any noticeable antifungal activity. The experimental results show that most of these complexes show antifungal activity at very high concentration, and on increasing concentration anti fungal activity also increases. In the case of benzilic acid alanine complexes shows that nikel complexes were found to be good inhibitor of phytophthora capsici and rhizoctinia solani. Cobalt complexes were moderate inhibitors. Results shows that all these complexes show antifungal activity at very high concentration and the increase in concentration increases the activity. But manganese and copper complexes don't have any noticeable antifungal activity against phytophthora capsici and rhizoctinia solani.

Now day's drug industries are looking for synthesizing the alternative compounds which act as very good antifungal agent. This study emphasis the special interest to the discovery of four thermally stable, new, metal complexes of benzilic acid-alanine which possess moderate antifungal activity.

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