

Studies on Metal Complexes of Thiazolines

Ritesh Kumar Mitra

Research Scholar

M.P.S. Science College Muzaffarpur

Dr. Birendra Prasad Singh

Supervisor

M.P.S. Science College Muzaffarpur

ABSTRACT:

This paper is deals with the preparation and characterisation of Fe (III), Fe(II), Co (II), Ni (II) and Cu (II) complexes of 2-Imino phenyl-3- phenyl-4 (p-methoxy phenyl)- Δ^4 - thiazoline and 2-Imino phenyl-3-phenyl-4(p-ethoxy phenyl)- Δ^4 -thiazoline. On the comparison of the spectra of ligand with these complexes it has been observed that most of the band had shifted. The band observed at 1635 cm^{-1} in the ligand assigned to $\nu(\text{C}=\text{N})$ practically remains unchanged on complexation. This shows that nitrogen of the thiazole ring does not take part in coordination. The band observed in the ligand in the region $740\text{--}680\text{ cm}^{-1}$ assigned to $\nu(\text{C}-\text{S})$ of thiazole ring shifted to lower frequency by $10\text{--}25\text{ cm}^{-1}$ giving an indication of the coordination of ring sulphur atom with the metal ion.

Key words: thiazole, thiazolines

INTRODUCTION:

Thiazolines and its derivatives have attracted the attention of several workers due to their wide range of activity.¹⁻⁸ Thiazoles are mainly used as analgesic, nematocides, bacteriocides and fungicides, while some of their compounds are used as local anesthetic⁹, antiviral¹⁰ and antiprotozoal¹¹ agents and above all as vulcanization accelerator¹² in rubber industry. The presence of $> \text{N}-\text{C}-\text{S}$ linkage, in the compounds, the toxicophoric importance of which has been documented in many fungicides¹³, have shown better fungicidal activities. Transition metal complexes formed by organic ligands are essential in plant nutrition, they have been widely studied which include several amines containing sulphur¹⁴ cystine and mercaptoacetate¹⁵. It has been reported in literature that metal complexes play an important role in biological activity of drugs. As complex formation has been suggested to one of the important mechanism for their vital action.¹⁶ Complexes containing thiazole and imidazole group as ligands are also of considerable interest because these groups form parts of several proteins which interact with the metal ions.

A recent review deals with the metal complexes of sulphur donor ligands and are of special attention due to their wide range of applicability and reactivity against protozoa, cancer, tuberculosis and certain kinds of tumour. Recently Srivastava et al¹⁷⁻²¹ have prepared a large number of transition metal complexes with oxazoles, oxazoline, thiazole and thiazoline and studied their structural and biological activity. Transition metal complexes of heterocyclic ligands²²⁻²⁸ have been prepared and characterised by several workers.

Large number of report appeared in the literature about the importance of mixed ligand complexes in the field of medicinal²⁹, analytical³⁰ and industrial chemistry³¹. The role of mixed ligand complexes in biological process has also been recognized³².

In the light of this view, the importance of metal complexes of sulphur donor ligands, we have reported a few Fe (II), Co (II), Ni (II) and Cu (II) complexes of 2-Imino-phenyl-3-phenyl-4 (p-methoxy/ ethoxy phenyl) - Δ^4 -thiazoline. In this chapter attempts have also been made to study their structure by elemental analysis, electronic spectra, and magnetic measurements. The fungicidal activity of ligands and their metal complexes were also determined against various fungi at different concentration.

EXPERIMENTAL:

All The chemicals used were of B.D.H. (A.R.) grade otherwise used after distillation. The methoxy /ethoxy acetophenone was obtained from Sisco lab. (Bombay).

The C, H, N and S were estimated from CDRI Lucknow and BHU. The I.R. and far I.R. were recorded in KBr or nuzollmull from G.N.D. Amritsar, Kurukshetra University and I.I.T. Delhi. Electronic (U.V). and T.G.A. were recorded from G.N.D. Amritsar.

The fungicidal activity was determined by the use of growth method at different concentration against various fungi viz. Phoma-exigue, Colletotrichum-capsicis Macrophomia- phaseoli.

The magnetic measurements were done at Roorkee University Roorkee at room temperature using mercury tetra thiocyanato cobaltate as calibrant.

[A] [PREPARATION OF THE LIGAND : 2-Imino-phenyl-3-phenyl-4-(p-methoxy/ethoxy phenyl) - Δ^4 -thiazoline]

The ligand was prepared according to the literature procedure.³³

The ligand was prepared from methoxy/ ethoxy acetophenone.

A solution of Br₂ (0.054 mole) in ethanol (40 ml) was added slowly with constant stirring to a solution of methoxy/ ethoxy aceto-phenone (0.051 mole) in ethanol (10ml) Sym- diphenyl thiourea (0.053 mole) was than added to above mixture. The reaction mixture was heated on a water bath using reflux condenser for 12 hours and finally for 4 hours without condenser. It was then kept in contact with ether for overnight to remove the unreacted ketone. Ether was removed by decantation. The product was then boiled with water (50 ml). The water was decanted hot and the residue obtained was treated with ammonia to triburated the free base and kept as such for overnight. The mass solidified this product was finally recrystallized from acetone. Analysis gave following influence as to their formulae.

| Ligands | % found/ Calculated | | | |
|---|---------------------|----------------|----------------|----------------|
| | C | H | N | S |
| C ₂₂ H ₁₈ N ₂ OS | 73.76 (73.74) | 5.06 (5.03) | 7.78 (7.82) | 8.88 (8.94) |
| C ₂₃ H ₂₀ N ₂ OS | 74.20 (74.19) | 5.40 (5.38) | 7.58 (7.53) | 8.56 (8.60) |

[B] PREPARATION AND ISOLATION OF METAL COMPLEXES:**(1) TRICHLORO/ TRIACETATO AND TRINITRATO TRIS (2-IMINO- PHENYL-3-PHENYL-4-(p METHOXY/ETHOXY PHENYL)- Δ^4 -THIAZOLINE Fe(III) COMPLEXES:**

These complexes have been synthesized by mixing ethanolic solution of ligand (0.03 mole) with Fe (III) salts (0.01 mole) in the same solvent under stirring and refluxed for two hours. The contents were concentrated and cooled. Brownish black crystals were obtained which were filtered washed thoroughly with ethanol and dried. The chemical analysis corresponds to the following molecular formulae.

| COMPLEX | % found / calculated | | | | |
|---|----------------------|----------------|----------------|----------------|----------------|
| | C | H | N | S | Fe |
| [Fe(C ₂₂ H ₁₈ N ₂ OS) ₃ Cl ₃] | 64.02 (64.10) | 4.40 (4.37) | 6.76 (6.79) | 7.72 (7.76) | 4.54 (4.53) |
| [Fe (C ₂₂ H ₁₈ N ₂ OS) ₃ (NO ₃) ₃ .H ₂ O] | 59.48 (59.47) | 4.19 (4.20) | 9.48 (9.46) | 7.22 (7.21) | 4.22 (4.20) |
| [Fe (C ₂₂ H ₁₈ N ₂ OS) ₃ (CH ₃ COO) ₃] | 66.06 (66.11) | 4.80 (4.82) | 6.42 (6.43) | 7.36 (7.35) | 4.30 (4.28) |
| [Fe (C ₂₃ H ₂₀ N ₂ OS) ₃ Cl ₃] | 64.76 (64.76) | 4.68 (4.69) | 6.58 (6.57) | 7.54 (7.51) | 4.36 (4.38) |
| [Fe(C ₂₃ H ₂₀ N ₂ OS) ₃ (NO ₃) ₃ .H ₂ O] | 60.24 (60.26) | 4.50 (4.51) | 9.20 (9.17) | 4.64 (4.66) | 4.06 (4.06) |
| [Fe (C ₂₃ H ₂₀ N ₂ OS) ₃ (CH ₃ COO) ₃] | 66.70 (66.72) | 5.16 (5.12) | 6.22 (6.23) | 7.16 (7.12) | 4.14 (4.15) |

2. [DICHLORO/ DINITRATO AND DIACETATO BIS (2-IMINO- PHENYL-3- PHENYL-4- (p-METHOXY/ ETHOXY PHENYL)- Δ^4 THIAZOLINE-Co (II) COMPLEXES].

Anhydrous Co (II) salts (0.01 moles) dissolved in minimum quantity of dry ethanol, were added to a solution of ligand (0.02 moles) also in minimum volume of ethanol. The pH of the reaction mixtures were slightly raised by addition of ammonia and the contents refluxed for one hour. On cooling the precipitates separate out, which were filtered, washed with ethanol and finally with ether, dried and analysed.

| COMPLEX | % found/Calculated | | | | |
|---|--------------------|----------------|----------------|----------------|----------------|
| | C | H | N | S | Co |
| [Co(C ₂₂ H ₁₈ N ₂ OS) ₂ Cl ₂] | 62.42 (62.41) | 4.24 (4.26) | 6.60 (6.62) | 7.58 (7.57) | 7.00 (6.97) |
| [Co(C ₂₂ H ₁₈ N ₂ OS) ₂ (NO ₃) ₂] | 58.72 (58.73) | 4.00 (4.01) | 9.28 (9.34) | 7.10 (7.12) | 6.58 (6.56) |
| [Co(C ₂₂ H ₁₈ N ₂ OS) ₂ (CH ₃ COO) ₂] | 64.52 (64.50) | 4.72 (4.70) | 6.30 (3.27) | 7.18 (7.17) | 6.62 (6.61) |
| [Co(C ₂₃ H ₂₀ N ₂ OS) ₂ Cl ₂] | 63.18 (63.16) | 4.56 (4.58) | 6.40 (6.41) | 7.30 (7.32) | 6.76 (6.75) |
| [Co(C ₂₃ H ₂₀ N ₂ OS) ₂ (NO ₃) ₂] | 59.54 (59.55) | 4.28 (4.31) | 9.00 (9.06) | 6.92 (6.90) | 6.40 (6.36) |
| [Co (C ₂₃ H ₂₀ N ₂ OS) ₂ (CH ₃ COO) ₂] | 65.16 (65.15) | 5.00 (4.99) | 6.00 (6.08) | 6.96 (6.95) | 6.42 (6.41) |

3. DICHLORO / DINITRATO AND DIACETATO BIS (2-IMINO- PHENYL-3- PHENYL-4-(p-METHOXY/ ETHOXY PHENYL)- Δ^4 -THIAZOLINE Ni (II) COMPLEXES:

The complexes were synthesized by adding ethanolic solution of the appropriate Ni (II) salts (0.01 mole) to a solution of ligand (0.02 mole) in ethanol, followed by the addition of alcoholic solution of sodium acetate. Reaction mixture were refluxed for one hour and they were concentrated to half of their volumes when precipitation occur. The precipitate so obtained were filtered, washed thoroughly with alcohol and finally with ether and dried. Elemental analysis corresponds to the following molecular formulae.

| COMPLEX | % found/ Calculated. | | | | |
|---|----------------------|----------------|----------------|----------------|----------------|
| | C | H | N | S | Ni |
| [Ni (C ₂₂ H ₁₈ N ₂ OS) ₂ Cl ₂ .2H ₂ O] | 60.00 (59.88) | 4.56 (4.54) | 6.38 (6.35) | 7.24 (7.26) | 6.64 (6.66) |
| [Ni (C ₂₂ H ₁₈ N ₂ OS) ₂ (NO ₃) ₂ .2H ₂ O] | 56.50 (56.49) | 4.30 (4.28) | 9.00 (8.99) | 6.86 (6.85) | 6.26 (6.28) |
| [Ni (C ₂₂ H ₁₈ N ₂ OS) ₂ (CH ₃ COO) ₂ .2H ₂ O] | 62.00 (62.02) | 4.96 (4.95) | 6.02 (6.03) | 6.88 (6.89) | 6.30 (6.32) |
| [Ni (C ₂₃ H ₂₀ N ₂ OS) ₂ Cl ₂ .2H ₂ O] | 60.65 (60.68) | 4.83 (4.84) | 6.20 (6.16) | 7.02 (7.04) | 6.40 (6.45) |
| [Ni (C ₂₃ H ₂₀ N ₂ OS) ₂ (NO ₃) ₂ .2H ₂ O] | 57.32 (57.34) | 4.56 (4.57) | 8.74 (8.73) | 6.66 (8.73) | 6.01 (6.09) |
| [Ni (C ₂₃ H ₂₀ N ₂ OS) ₂ (CH ₃ COO) ₂ .2H ₂ O] | 62.73 (62.72) | 5.86 (5.85) | 5.86 (5.85) | 6.70 (6.69) | 6.10 (6.14) |

4. DICHLORO/ DINITRATO AND DIACETATO BIS (2 IMINO-PHENYL- 3-PHENYL-4- (p-METHOXY / ETHOXY PHENYL)- Δ^4 - THIAZOLINE Cu (II) COMPLEXES:

An alcoholic solution of ligand (0.02 mole) was mixed with an aqueous solution of corresponding Cu (II) salts (0.01 mole). Few drop of dil. ammonia solution was added to obtain the desired pH and then the reaction mixture were refluxed for one hour. The precipitates obtained on cooling were filtered, washed with water, ethanol and finally with diethyl ether the complexes were dried and the analysed.

| COMPLEX | % found/ Calculated. | | | | |
|---|----------------------|----------------|----------------|----------------|----------------|
| | C | H | N | S | Cu |
| [Cu (C ₂₂ H ₁₈ N ₂ OS) ₂ Cl ₂] | 62.02 (62.04) | 4.22 (4.23) | 6.56 (6.58) | 7.50 (7.52) | 7.50 (7.52) |
| [Cu (C ₂₂ H ₁₈ N ₂ OS) ₂ (NO ₃) ₂] | 58.40 (58.41) | 4.00 (3.98) | 9.30 (9.29) | 7.06 (7.08) | 7.06 (7.08) |
| [Cu (C ₂₂ H ₁₈ N ₂ OS) ₂ (CH ₃ COO) ₂] | 64.12 (64.14) | 4.66 (4.68) | 6.22 (6.24) | 7.12 (7.13) | 7.12 (7.13) |
| [Cu (C ₂₃ H ₂₀ N ₂ OS) ₂ Cl ₂] | 62.80 (62.79) | 4.54 (4.55) | 6.34 (6.37) | 7.26 (7.28) | 7.26 (7.28) |
| [Cu (C ₂₃ H ₂₀ N ₂ OS) ₂ (NO ₃) ₂] | 59.22 (59.23) | 4.30 (4.29) | 9.00 (9.01) | 6.86 (6.87) | 6.86 (6.87) |
| [Cu (C ₂₃ H ₂₀ N ₂ OS) ₂ (CH ₃ COO) ₂] | 64.80 (64.79) | 4.98 (4.97) | 6.03 (6.05) | 6.92 (6.91) | 6.92 (6.91) |

5. 4 DICHLORO / DINITRATO AND DIACETATO BIS (2 IMINO-PHENYL- 3-PHENYL-4- (p-METHOXY / ETHOXY PHENYL)- Δ^4 - THIAZOLINE Fe (II) COMPLEXES]:

The complexes were prepared by refluxing for two hours the respective Fe (II) salts with ligand in 1:2 molar ratio in aqueous ethanolic medium. On concentrating the complexes so formed were suctioned filtered, washed with alcohol, ether and dried in vacuo. The chemical analysis correspond to the following molecular formulae.

| COMPLEX | % found/ Calculated. | | | | |
|--|----------------------|----------------|----------------|----------------|----------------|
| | C | H | N | S | Fe |
| [Fe (C ₂₂ H ₁₈ N ₂ OS) ₂ Cl ₂ 2H ₂ O] | 60.06 (60.07) | 4.52 (4.55) | 6.38 (6.37) | 7.30 (7.28) | 6.36 (6.37) |
| [Fe (C ₂₂ H ₁₈ N ₂ OS) ₂ (NO ₃) ₂ 2H ₂ O] | 56.64 (56.65) | 4.28 (4.29) | 9.00 (9.01) | 6.86 (6.87) | 6.00 (6.01) |
| [Fe (C ₂₂ H ₁₈ N ₂ OS) ₂ (CH ₃ COO) ₂ 2H ₂ O] | 62.21 (62.20) | 4.50 (4.97) | 6.02 (6.05) | 6.98 (6.91) | 6.04 (6.05) |
| [Fe (C ₂₃ H ₂₀ N ₂ OS) ₂ Cl ₂ 2H ₂ O] | 60.84 (60.86) | 4.86 (4.85) | 6.14 (6.17) | 7.02 (7.06) | 6.20 (6.17) |
| [Fe (C ₂₃ H ₂₀ N ₂ OS) ₂ (NO ₃) ₂ 2H ₂ O] | 57.52 (57.50) | 4.60 (4.58) | 8.76 (8.75) | 6.63 (6.67) | 5.84 (5.83) |
| [Fe (C ₂₃ H ₂₀ N ₂ OS) ₂ (CH ₃ COO) ₂ 2H ₂ O] | 62.88 (62.89) | 5.22 (5.24) | 5.82 (5.87) | 6.70 (6.71) | 5.81 (5.87) |

INFRA-RED SPECTRAL STUDIES:

In the I.R. spectra a number of absorption bands with varying intensities were obtained in the ligand and its metal complexes. The ligand has absorption bands in the region 1530-1595, 1495 and 1405 cm⁻¹ characteristics of five membered thiazole ring. However, the main absorption bands in the ligand lie in the region 1630, 3095 and 1695-1470 cm⁻¹ assignable to γ (C=C), γ (C-H) and the conjugated cyclic system (-C=C-N-C-) respectively γ (C=N) of thiazoles which are similar to these of Schiff's bases and oximes where it occur³⁴ in the range 1475-1680 cm⁻¹. In the present ligand the band appears at 1640 cm⁻¹ remain unchanged during complexation. In addition, the ligand has several bands in the 640-1505 cm⁻¹ region probably due to coupled (C-

S) and (C-N) vibrations³⁴, occurring near 1460-1485 cm^{-1} and 653 cm^{-1} respectively. While a band probably due to the combined effect of γ (C=N) + γ (C-N) appear at 1295-1325 cm^{-1} which does not show any shift in the spectra of complexes indicating its non-coordination. The phenyl and methyl ring vibrations³⁵ have been observed in the region 1595-1605 and 1340-1365 cm^{-1} respectively. On comparing the spectra of metal complexes with those of ligands it has been observed that frequency associated with γ (C-S) stretching mode shifts to lower range by 1025 cm^{-1} , giving an indication that the coordination of ring sulphur atom with the metal ion. In the present complexes the various vibration mode due to γ (M-S) stretching frequencies were observed in the region 280-305, 290-335, 285- 335 and 290-340 cm^{-1} which may be assigned to γ (Fe-S) γ (Co-S), γ (Ni-S) and γ (Cu-S) stretching vibrations respectively.

INFRA RED SPECTRA OF CHLORO COMPLEXES:

The bands present in the region 260-275 cm^{-1} due to γ (Fe-Cl) are well in agreement for six- coordinate halide bridge vibrations.³⁶ While the bands of medium intensity appear near 295 cm^{-1} which can be assigned to γ (Co-Cl) stretching frequencies. However, the bands present at 285 cm^{-1} due to γ (Ni-Cl) support the octahedral geometry of the Ni (II) complexes. The band observed at 295-305 cm^{-1} is due to γ (Cu-Cl) indicate the square - planar structure. In the case of distorted octahedral geometry the band is always formed at lower frequencies.

INFRA-RED SPECTRA OF ACETATO COMPLEXES :

Two bands were observed in the case of acetato complexes are at 1540-1565 and other at 1430-1445 cm^{-1} which may be assigned to asymmetric and symmetric (-COO) stretching vibrations respectively. The separation of 110-125 cm^{-1} in these modes on complexation suggests that the acetato group is behaving as unidentate ligand in these complexes.

INFRA RED SPECTRA OF NITRATO COMPLEXES:

The nitrate group has D_{3h} symmetry in free ion and has three infra- red active vibrations such as γ_2 (825- cm^{-1}), γ_3 (1385 cm^{-1}) and γ_4 (~ 705 cm^{-1}). Assignments of γ_1 at 1455-1430, γ_2 at 1045-1030 and γ_6 at 810-830 cm^{-1} agree well with the published values for coordinated nitrate group in Fe (III), Co (II), Ni (II) and Cu (II) complexes. The strong bands at 745-730, 1285-1260 and 710-720 cm^{-1} can be assigned to γ_3 , γ_4 and γ_5 modes, respectively. Furthermore γ_1 and γ_4 vibrations were found to be separated by 175 cm^{-1} . Although the size of the splitting is not a good criterion for distinguishing mono- or bidentate nitrate groups, yet the values are in agreement with bidentate chelating nature of bridging M-O (NO)-O-M nitrate groups.

MAGNETIC MOMENT AND ELECTRONIC SPECTRAL STUDIES:

The present work is an attempt in the direction of seeking a correlation between magnetic moment and ligand field parameters.

Fe (III) Complexes:

The magnetic moment of Fe (II) complexes observed at room temperature lie in the range 5.62-5.65 B.M. The value is however, suggestive of high- spin six coordinated Fe (III) complexes

The octahedral Fe (III) complexes exhibit broad bands assignable to ${}^5T_{2g} \rightarrow {}^5E_g$ transition. Here two bands are observed near 8650 and 10550 cm^{-1} which are split components of one band assignable to ${}^5T_{2g} \rightarrow {}^5E_g$. This splitting of the E_g state may be due to distortion of the octahedron since tetragonal and rhombic distortion split 5E_g excited state but static distortion of the octahedron is not expected to occur for a variety of electronic reasons, in the molecules having T_{2g} ground state. The possibility of trigonal distortion is not anticipated because such a distortion would not warrant the lifting of degeneracy of 5E_g states. Thus in this case it appears that the splitting of spin- allowed band is attributed only to Jahn- Teller effect and all other explanations seen to be invalid.

Co (II) Complexes:

The theory of magnetic susceptibility of Co (II) was given originally by Schalp and Penney while the best summary of recent results is given by Figgis Nyholm. The observed value of magnetic moment 4.40-4.45 B.M.

at room temperature lie well with in the range expected for tetrahedral Co (II) complexes and are generally diagnostic of the coordination geometry around the metal ion.

The spectra of present Co (II) complexes were very similar and three spin- allowed transitions ${}^4A_2 \rightarrow {}^4T_2$ (γ_1), ${}^4A_2 \rightarrow {}^4T_1$ (F) (γ_2), and ${}^4A_2 \rightarrow {}^4T_1$ (P) (γ_3), are expected to occur in tetrahedral field. The reflectance spectra exhibits bands at 19000-19250, 16050, 8700-8850 and 7050 cm^{-1} in conformity with the spectra of other tetrahedral Co (II) complexes. The doublet in the region 7000- 8850 is assigned to the split component of γ_2 transition. The doublet in the visible region with maxima at 19250 and 16050 can be assigned to the split components of the γ_3 transitions. Using the method of Cotton Good game various crystal field parameters for Co (II) complexes have been calculated.

Ni (II) Complexes:

The present six- coordinated Ni(II) complexes exhibit a magnetic moment 2.80-3.10 B.M. expected for two unpaired electrons in an octahedral field.⁴⁶ The electronic spectra indicates an octahedral or tetragonal arrangements of the ligands. Although the complexes formally have D_{4h} symmetry, the electronic spectra in the range 8000-8350 cm^{-1} and magnetic moment values are typical of octahedrally coordinated Ni (II) complexes the observed energies of three spin- allowed transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$ at 8400-8750, ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) at 14000 – 14100 and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) at 24000-24150 cm^{-1} agree well with those predicted from Liehe and Ballhausen energy level diagram for Ni (II) in a ligand field of octahedral symmetry. The ligand filed parameters $10 Dq$ was taken equal to the observed energy of the first triplet transition (γ_1) and the Racah parameter B was calculated by substitution of (γ_1), (γ_2) and (γ_3) band energies in the secular equation. Furthermore, observed value of 1.61-1.66 for ratio (γ_2/γ_1) are in accord with commonly reported value of 1.60-1.70 for Ni (II) complexes of octahedral symmetry.

Cu(II) Complexes:

The room temperature magnetic moment for the present complexes have been found in the range 1.50-1.52 B.M. which is lower than the spin only value of 1.73 B.M. required for an $S=1/2$ system. Some what subnormal magnetic moment values can be attributed to the anti ferromagnetic exchange between the interacting Cu^{+2} ions, thus dimidiation or polymerization in the solid state either through Cu^{+2} - Cu^{+2} interaction or through ligand participation cannot be ruled out in the present case.

The square planer geometry have been confirmed by the nature of absorption bands which appear in the visible spectra of the complexes. Two bands have been observed in their electronic spectra in the region 15300-15600 and 19200-19300 cm^{-1} which may be attributed to d-d transition ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and $2B_{1g} \rightarrow {}^2E_g$ respectively in a planer field. Distortion of the planer complexes towards a tetrahedral configuration lowers the band frequency. Bands at 10050 and 13850-12000 cm^{-1} have been assigned from their frequency and relatively low intensities to crystal field transition of Cu(II) in a pseudo tetrahedral environment. Hence the absence of a band below 10050 cm^{-1} in these complexes eliminates the possibility of tetrahedral structure. However, a distorted, effectively planer structure is likely as the ${}^3B_{1g} \rightarrow {}^3E_g$ transition is likely to be more intense.

FUNGICIDAL ACTIVITY:

A number of organic and inorganic compounds containing sulphur atoms are known which acts as fungicides and pesticides. Young and Deong studied the properties of colloidal sulphur as insecticides and a variety of hydrophobic and hydrophylic sulphur compounds were prepared.

Roark and Cotton, Hertzell and Willcoxon as well as Moore mentioned derivatives of thiocyanate for their strong pesticides action.

The mechanism of action of sulphur containing ligands and their metal complexes has been a subject of interest for many years. It is presumed that sulphur compounds acts as hydrogen acceptor in metabolic system and in doing so, disturb the normal hydrogenation and dehydrogenation reaction in the fungal cells. The views are however based on the presumption that sulphur being next to oxygen, acts much like oxygen. The work of Tweedy however suggests that the cytochrome system is involved in the reduction of sulphur compounds. Owens advocated an interesting theory and suggested that reaction polysulphide free radicals might form stable

cross linkages with protein and other cellular compounds of fungus. This theory however provides one of the most intriguing unsolved problems in fungicidal mechanism.

The thiazolines and its Fe (III), Co (II), Ni (II) and Cu (II) complexes have been assayed for their fungicidal action against *Phoma-exigua* *Macrophomia- phascoli* and *Colletotrichum-Capsici* at different concentrations 100, 50 and 20 ppm. and an attempt has been made to establish a relationship between fungicidal activity and chemical structure.

The result obtained shows that there exists a gradual decline of growth with the increasing dose of the complexes. The ligand possesses good fungicidal activity which seems to be related with the size of substituents. The ligand exhibit greater activity in comparison to its complexes which might be due to the fact that the ligand in the Free State can easily combine with fungal cells and check their growth. However on complex formation adduct compounds are formed. Solubility of the complexes also constitutes an important factor responsible for the biological activity. The ligand, because of its strongly soluble nature in acetone and alcohol can be easily absorbed by fungal hyphae but the complexes are not much soluble which accounts for the differences in toxicity between the ligand and the complexes. The analysis of the results showed that among all the metal complexes screened for their fungicidal activity against the three fungi, Cu (II), complexes seem to be most active fungicides. The toxicity of metal ions in the decreasing order has been observed in the following manners :

Cu (II) > Ni (II) > Co (II) > Fe (III)

Again from the data of toxicological studies, it is observed that 1:2 complexes are more active than 1:3 complexes.

The anions attached to metal complexes also govern the result to some extent. In case of Ni (II) and Co (II) complexes the nitrate complexes are most effective, next in order of efficiency where the acetato complexes while in Cu (II) and Fe (III) complexes the order of toxicity as $Cl^- > NO_3^- > CH_3 COO^-$ were observed most effective.

REFERENCES

- H. Tripathy, R.N. Dash B.C. Dash and G.N. Mahapatra *Ind. J. Chem.*, **9**, 1232 (1971)
- A. Burger and S.N. Sawhney *J. Med. Chem.*, **11**, 270 (1968)
- D.L. Garmaise, C.H. Charmbars and R.C. Mecral *J. Med. Chem.*, **11**, 1205 (2005).
- B.C. Dash, G.N. Mahapatra *J. Proc. Inst. Chemists, India*, **34**, 178 (19670)
- U. Yoshiro *Ann. Rep. Res. Lab.*, **27**, 112 (1968)
- K.S.L. Srivastava *Allg. Prakt. Chem.*, **19**, 398 (1987)
- J.M. Singh and B.N. Tripathy *J Ind. Chem. Soc.*, **47**, 23 (1970)
- V.S. Misra and A. Saxena *J Prak. Chem.*, **36**, 260 (2002)
- T. Vitali, F. Mossini, G. Bertacine and M. Impiciatone , *Farmaco* *Ed. Sci*, **23**, 1081 (1968)
- N.P. Buhoi G. Saintruf J.C. Perche and J.C. Bourgade *Chim. Ther.*, **3**, 110 (1968)
- M. Avaramoff S. Alder and A. Foner *J. Med. Chem.* **10**, 1138 (1967)
- C. Thibavlt and A. Danche *Fr. Pat*, **1**, 510-015, June 19, 1968.
- M.C. Goldsworthy E.L. Green and M.A. Smith *J. Agr. Reserach*, **66** 277 (1943)
- E. Conick, W.C. Fermelius *Ibid*, **76**, 4671 (1954)
- Q. Fernando and H. Friliser *J. Am. Chem. Soc.* , **80**, 4180 (1958)
- C.D. Coryell *Special problems in the formation of metal complexes in chemical specificity in biological interactions*, edited by R.N. Gurd (Academic Press, New York) **90**, (1954)
- Srivastava, S.K. Verman A, & Gupta, A. *J. Indian Chem. Soc* **LIX 925** (1982)
- Srivastava, S.K. Gupta A, & Verman, A. *Chhemical Indica Acta Turcia* **11**, 99 (1983)
- Srivastava S.K. Gupta A & Verman. A. *Egyptian Journal of Chem* **26**, 173 (1983)
- Srivastava S.K., Gupta, A. *Acta Chemical Hungry* **48**, 42 (1985)

21. Issa, Y.M., Rizk, M.S. Abdul Ghani, N. T and Atwa, S.M. J. Indian Chem. Soc. **71**, 575 (1994)
22. Ghoshal, M.N and Chawan, M.C. Asian J. Chem **10** (4), 951 (1998)
23. Singh, L. Tyagi Neelam and Dhaka, N.P. Asian J. Chem. **10** (4) 915 (1998)
24. Pokhariyal G.P. and Singh P. J. Indian Chem. Soc. **64**, 501 (1987)
25. Awadallah R.M., Mehammed A.E. and Ramadan A.M. J. Indian Chem., Soc, **65**, 532 (1988)
26. Issa Y.M., Rizk M.S. Abdul Ghani N.T. and Atula S.M. J. Indian Chem. Soc. **71**, 575 (1994)
27. M.A. Ali Qurashi and A.A.M. Ali J. Indian Chem. Soc., **72**, 431 (1995)
28. Sharnda K. Nalanda J. Indian Chem. Soc. **72**, 439, (1995)
- Gonorkai M. C and Rao N
29. Chakraborty J. and Patel R.N. J. Indian Chem. Soc. **73**, 191 (1996)
30. Chattopadhyay P. Dolui B.K. Indian J. Chem. **36 A**, 419 (1997)
31. Nag J.K. Das de B.B. J. Indian Chem. Soc **75**, 496 (1998)
32. Kriza A., et al. J. Indian Chem. Soc. **77**, 83 (2000)
16. Srivastava, S.K. Verma A, & Gupta, A. J. Indian Chem. Soc **LIX 925** (1982)
17. Srivastava, S.K. Gupta A, & Verma, A. Chhemical Indica Acta Turcia **11**, 99 (1983)
18. Srivastava S.K. Gupta A & Verma. A. Egyptian Journal of Chem **26**, 173 (1983)
19. Srivastava S.K., Gupta, A. Acta Chemical Hungry **48**, 42 (1985)
20. Issa, Y.M., Rizk, M.S. Abdul Ghani, N. T and Atwa, S.M. J. Indian Chem. Soc. **71**, 575 (1994)
21. Ghoshal, M.N and Chawan, M.C. Asian J. Chem **10** (4), 951 (1998)
22. Singh, L. Tyagi Neelam and Dhaka, N.P. Asian J. Chem. **10** (4) 915 (1998)
23. Pokhariyal G.P. and Singh P. J. Indian Chem. Soc. **64**, 501 (1987)
24. Awadallah R.M., Mehammed A.E. and Ramadan A.M. J. Indian Chem., Soc, **65**, 532 (1988)
25. Issa Y.M., Rizk M.S. Abdul Ghani N.T. and Atula S.M. J. Indian Chem. Soc. **71**, 575 (1994)
26. M.A. Ali Qurashi and A.A.M. Ali J. Indian Chem. Soc., **72**, 431 (1995)
27. Sharnda K. Nalanda J. Indian Chem. Soc. **72**, 439, (1995)
- Gonorkai M. C and Rao N
28. Chakraborty J. and Patel R.N. J. Indian Chem. Soc. **73**, 191 (1996)
29. Chattopadhyay P. Dolui B.K. Indian J. Chem. **36 A**, 419 (1997)
30. Nag J.K. Das de B.B. J. Indian Chem. Soc **75**, 496 (1998)
31. Kriza A., et al. J. Indian Chem. Soc. **77**, 83 (2000)
32. H. Tripathi, P.N. Dhal and G.N. Mahapatra J. Ind. Chem. Soc., **50**, 135 (1973)
33. R.M. Silversterin and G.C. Bassler Spectrometric Indentification of organic compounds (John Wiley New York) 1367 (1968)
34. J. Miyazawa, T. Shimanouchi and S. Mizushima J. Phys. Chem., **29**, 611 (1958)
35. B.S. Sandhu, J.N. Kumaria, J. Singh and N.S. Saxena J. Ind. Chem., Soc., **53**, 114 (2005)