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SYNTHESIS OF THIAZOLINE COMPLEXES OF Cu (II), Ni (II) AND Co (II) TRANSITION METALS

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Abstract: -

The synthesis and characterization (elemental analysis, IR, electronic and magnetic susceptibility studies) of the transition metal complexes of Ni (II), Co (II) and Cu (II) with 2 - amino -4- (p- methoxy phenyl) thiazoline is described and complexes are obtained in 75-78% yield from the treatment of metal salts with ligand 2-amino4-(p-methoxy phenyl) thiazoline in 1:2 molar ratio in ethanolic medium. From the analytical and spectral data the stoichiometry of these complexes have been found to be of the type ML_2X_2 (where M = Cu (II), Co (II) and Ni (II)}.Evidences indicate that Ni(II), Cu(II) and Co(II) complexes exhibit octahedral and square planar geometry.

The fungicidal activities of ligands and metal complexes were screened by growth method against various fungi i.e. Dreschlere setramera, Fusarium oxysporum, Macrophomera phaseoli at different concentrations. It is found that the activity decreases with decrease of concentration and the metal complexes are less toxic than the parent ligand.

Key words: *Thiazoline Complexes, Electronic Studies, Fungicidal Activity, Heterocyclic Compounds, Toxicity.*

INTRODUCTION

A considerable number of transition metal complexes with heterocylic ligands in which the later behave as monodentate N-bonded and sometimes bridging N-ring or S-ring bonded have been investigated. Thiazoles and their thiazoline analogues are well known to coordinate to transition metal fragments and a large number of such compounds have been isolated that can potentially ligate transition metals. Complexes of transition metals ions containing ligands with N, S and N, S, O donors are known to exhibit interesting stereo chemical, electrochemical and electronic properties. Transition metal complex formed by organic ligands are essential in plant nutrition, they have been studied which induced several amines containing sulphur and mercaptoacetates. Thiazolines and their derivatives have created an interest due to their wide range of activity. Thiazoline and their derivatives possess anti-malarial, anti-theminitic, anti-fungal, anti-bacterial and anti-tubercular activities. Such compounds can also be used as local anesthetic, anti-radiation drugs, anti-viral and anti-protozoan agents and also in the rubber industry as vulcanization accelerators. The synthesis, spectral characterization and biological activity of Schiff's base derived metal complexes were studied by many workers [1-2]. Similar experiments on fungicidal and antimicrobial activities of Cu (II), Co (II) and Ni (II) Complexes with O, N, and S donor, their EPR and electronic spectral studies were also conducted by many workers [3-8] Schiff's base derived complexes of derivatives of DHA, their spectra and synthesis under microwave irradiation were also studied by many workers [9.10]. Attempts have been made to study their structure with the help of elemental analysis, magnetic measurements, spectral studies and conductance measurements. The present paper deals with the preparation and characterization of Cu(II), Co(II) and Ni(II) complexes with 2-amino-4-(p-methoxy phenyl) thiazoline ligand. Metal complexes play an important role in biological activity. In many cases metal complexes are more potent than free ligands. These newly synthesized complexes were also screened for their antifungal activity against fungi viz. Drechslera-tetramera, Fusarium-oxysporum and Macrophomera-phoseoli at different concentrations [11].

EXPERIMENTAL

MATERIALS AND METHODS:

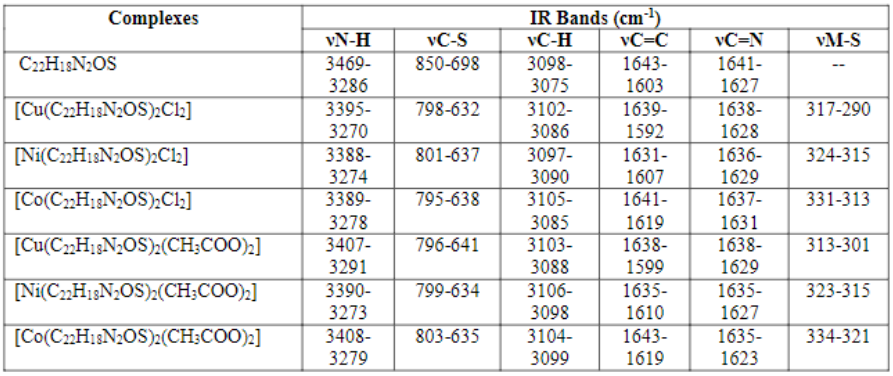
All the chemicals and reagents used were of analytical grade; otherwise they were purified before use. Organic solvent used was absolute alcohol. IR spectra of the ligand and complexes are recorded in nujolmull. The fungicidal activity of ligands as well as complexes was determined by using the Growth method. The electronic spectra were recorded in MgO at room temperature on VSU-22 spectrophotometer. The measurements were carried out Guru Nanak Dev University, Amritsar. Metal and sulphur contents of these complexes were estimated using the standard procedures reported in literature [12,13]. The estimation of carbon, hydrogen, sulphur and nitrogen were carried out at BHU, Varanasi and CDRI, Lucknow and results are given in Table 1. Magnetic measurements were carried out at IIT Roorkee at room temperature using Co [Hg $(CNS)_4$] as a calibrant.

TABLE 1 ELEMENTAL ANALYSIS DATA

Complexes	%Calc./ Obs.					
	C	H	S	N	O	M
C22H18N2OS	73.74 73.71	5.02 5.01	8.93 8.86	7.82 7.71	4.46 4.39	-----
$[Cu(C_{22}H_{18}N_2OS)_2Cl_2]$	62.08 62.06	4.20 4.14	7.50 7.42	6.51 6.48	3.70 3.66	7.40 7.41
$[Ni(C_{22}H_{18}N_2OS)_2Cl_2]$	62.40 62.42	4.20 4.19	7.52 7.42	6.60 6.62	3.70 3.84	6.90 6.81
$[Co(C_{22}H_{18}N_2OS)_2Cl_2]$	62.40 62.33	4.20 4.12	7.50 7.46	6.60 6.51	3.70 3.64	6.90 6.86
$[Cu(C_{22}H_{18}N_2OS)_2(CH_3COO)_2]$	64.10 64.02	4.60 4.55	7.10 7.07	6.20 6.16	10.60 10.53	7.67 6.63
$[Ni(C_{22}H_{18}N_2OS)_2(CH_3COO)_2]$	64.50 64.42	4.70 4.65	7.10 7.04	6.20 6.16	10.70 10.63	6.60 6.58
$[Co(C_{22}H_{18}N_2OS)_2(CH_3COO)_2]$	64.52 64.44	4.68 4.62	7.13 7.11	6.19 6.16	10.72 10.66	6.61 6.58

The ligand 2-amino-4-(p-methoxy phenyl) thiazoline was prepared using the procedure reported in the literature [14].

TABLE 2
CHARACTERISTIC IR BANDS OF LIGANDS AND COMPLEXES



Complexes	IR Bands (cm^{-1})					
	νN-H	νC-S	νC-H	νC=C	νC=N	νM-S
$C_{22}H_{18}N_2OS$	3469-3286	850-698	3098-3075	1643-1603	1641-1627	--
$[Cu(C_{22}H_{18}N_2OS)_2Cl_2]$	3395-3270	798-632	3102-3086	1639-1592	1638-1628	317-290
$[Ni(C_{22}H_{18}N_2OS)_2Cl_2]$	3388-3274	801-637	3097-3090	1631-1607	1636-1629	324-315
$[Co(C_{22}H_{18}N_2OS)_2Cl_2]$	3389-3278	795-638	3105-3085	1641-1619	1637-1631	331-313
$[Cu(C_{22}H_{18}N_2OS)_2(CH_3COO)_2]$	3407-3291	796-641	3103-3088	1638-1599	1638-1629	313-301
$[Ni(C_{22}H_{18}N_2OS)_2(CH_3COO)_2]$	3390-3273	799-634	3106-3098	1635-1610	1635-1627	323-315
$[Co(C_{22}H_{18}N_2OS)_2(CH_3COO)_2]$	3408-3279	803-635	3104-3099	1643-1619	1635-1623	334-321

A shift in the νC-S and νN-H band frequencies is observed in all the complexes. This shows that the lone pair of electron presents on the sulphur atom of thiazoline ring and nitrogen atom of free amino group is taking part in co-ordination (Table 2).

TABLE 3
(a) ELECTRONIC REFLECTANCE SPECTRAL DATA AND THEIR ASSIGNMENTS OF NI(II) COMPLEX

Complexes	ν1	ν2	ν3	Dq	B	ν2/ ν1	$ν_3$(Calc.)
$[Ni(C_{22}H_{18}N_2OS)_2Cl_2]$	8520	14520	24451	1285.4	600	1.70	28968
$[Ni(C_{22}H_{18}N_2OS)_2(CH_3COO)_2]$	8512	14511	24419	1283.6	662.4	1.70	28999

$ν_1 = {}^3A_{2g}$ (F) → ${}^3T_{2g}$ (F), $ν_2 = {}^3A_{2g}$ (F) → ${}^3T_{1g}$ (F) and $ν_3 = {}^3A_{2g}$ (F) → ${}^3T_{1g}$ (P).

(b) ELECTRONIC REFLECTANCE SPECTRAL DATA AND THEIR ASSIGNMENTS OF CO(II) COMPLEX

Complexes	ν1	ν2	ν3	Dq	B	ν2/ ν1	$ν_2$(Calc.)
$[Co(C_{22}H_{18}N_2OS)_2Cl_2]$	8819	14246	20082	1198.2	667	1.61	27226
$[Co(C_{22}H_{18}N_2OS)_2(CH_3COO)_2]$	8798	14244	20041	1195.3	666	1.61	27199

ν1 = 4T1g (F) → 4T2g(F), ν2 = 4T1g (F) → 4A2g (F) and ν3 = 4T1g (F) → 4T1g (P).

(c) ELECTRONIC REFLECTANCE SPECTRAL DATA AND THEIR ASSIGNMENTS OF CU(II) COMPLEX

Complexes	ν1	ν2	ν3	Dq	B	ν2/ ν1	$ν_2$(Calc.)
$[Cu(C_{22}H_{18}N_2OS)_2Cl_2]$	15327	19121	--	--	--	--	--
$[Cu(C_{22}H_{18}N_2OS)_2(CH_3COO)_2]$	15325	19128	--	--	--	--	--

ν1 =2B1g → 2A1g and ν2 = 2B1g → 2Eg
CZ-record UV-Viz. spectrometer provided with an automatic recorder was used to record the electronic spectra of the complexes in ethanol at room temperature (Table 3).

PREPARATION OF METAL COMPLEXES

In general all these complexes were synthesized by refluxing the respective metal salts with ligand 2-amino-4(p-methoxy phenyl) thiazoline in 1:2 molar ratio in ethanolic medium on water bath for one hour. The solution was concentrated to half of its volume then it was kept for some time. The crystals of complexes separated out which were filtered, washed with alcohol and dried in vacuum. Similarly some complexes of thiazoline were also synthesized by many workers [15-21].

RESULTS AND DISCUSSION

Adducts of all the complexes were prepared by refluxing the respective metal salts with ligands in 1:2 molar ratio in ethanolic medium. The crystals of complexes separated out which were filtered, washed with alcohol and dried in vacuum.
IR Studies: The ν (C=N) band frequencies in the free ligand are completely unaffected on complexation. The unchanged position of the band indicates that the ring nitrogen does not take any part in the coordination. The band observed at 850-698 cm^{-1} in the free ligand assigned to asymmetric ν(C-S) is shifted to lower frequency after complexation. But the symmetric ν (C-S) frequency completely disappears or intensity of this band is reduced after complexation. These facts confirm that the ring sulphur is taking part in complex formation. The ν(N-H) asymmetric and symmetric stretching frequencies appearing in the region 3469 and 3286 cm^{-1} respectively, also decreases in the complex. This shows that the lone pair of electron available on nitrogen atom took part in coordination. From the above observation it is clear that the nitrogen of the –NH_2 group and ring sulphur take part in coordination.

Electronic Reflectance Spectral Studies:

In the electronic spectra of Ni (II) complexes three bands at 8512-8520, 14511-14520 and 24419-24451 cm^{-1} were observed which may be assigned for $^3A_{2g}$ (F) → $^3T_{2g}$ (F) (ν_1), $^3A_{2g}$ (F) → $^3T_{1g}$ (F) (ν_2) and $^3A_{2g}$ (F) → $^3T_{1g}$ (P) (ν_3) which are characteristic of octahedral Ni(II) ion. The magnetic moment values are found in the range 2.90-3.20 B.M. This is in support of high spin octahedral complex. The value is however is raised only to a small extent suggesting that the splitting is weak and that the environment is quite close to an octahedral one [22].

The observed value of magnetic moment is found in the range 2.97-3.55 B.M. which is expected for octahedral Co (II) complex. Three bands were observed at 8798-8819, 14244-14246 and 20041-20082 cm^{-1} which may be assigned to $^4T_{1g}$ (F) → $^4T_{2g}$ (F) (ν_1), $^4T_{1g}$ (F) → $^4A_{2g}$ (F) (ν_2) and $^4T_{1g}$ (F) → $^4T_{1g}$ (P) (ν_3) respectively for octahedral complexes.

Two bands were observed in the electronic spectra of Cu (II) complexes in the region 15325-15327 and 19121-19128 cm^{-1} which may be assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ respectively in a planar field. The magnetic moment value foe the Cu (II) complexes lie in the range 1.54-1.58 B.M. which support square planar geometry.

The fungicidal activities of the ligand as well as of metal complexes were screened against different fungi at different concentrations 100, 50 and 20 ppm in Czapek's dox agar medium. It has been observed that the fugitoxicity of the metal complexes are lesser than the free ligand. This might be due to the fact that the group which is responsible for toxicity is not free in complexes due to co-ordination however it is free in ligand. The ligand as well as the metal complexes is most toxic at higher concentration i.e. the fungicidal activity decreases with the decrease of concentration.

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