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Synthetic and Spectroscopic Studies of Co(II) Complexes of Thiohydrazides and Pyridine Carboxylic Acid

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ABSTRACT

Sulphur containing compounds are found to be most effective radioprotective agents in vitro and vivo. The mode of action of these compounds in modifying the radiation effects is generally thought to be a combination of the processes- (i) Scavenging of potentially damaging primary water radicals and (ii) repair of damaged molecules by transfer of a hydrogen atom from the SH group. Also the increasing commercial value of transition metal complexes with sulphur donor ligands has created much interest in the field of Chemistry. A large number of hydrazides and hydrazones (Alcock et al., 1972) have shown significant amoebicidal activities. Salicylic acid hydrazide is particularly important due to its anti tuberculous (Katyal and Datt, 1975) antipyretic fungistatic and diuretic (Perkins et al., 1990) activities. Thus there has been considerable interest in the Chemistry of acid hydrazides and hydrazones because of their use in biological systems (Bhirud and Srivastava, 1990, Alcock et al., 1972, Katyal and Datt, 1975). The complexes of N-acetylpyridine–N'–2–thiophene–thiocarboxyhydrazide and pyridine carboxylic acid with heavy metal Co(II) have been synthesized. The chelates have been characterized on the basis of elemental analysis, magnetic behavior, IR, reflectance spectral studies and thermodynamic parameters calculated by using thermogravimeteric analysis (TGA) and differential thermal analysis (DTA). The anti bacterial and anti fungicidal activities were tested. The complexes of Co(II) with different ligands and co-ligands exhibit appreciable anti bacterial and anti fungicidal activities against S.aureus, B.megaterium, B.cereus and E.coli.

Keywords: Acylthiohydrazides, Anti Bacterial, Anti Fungicidal, IR, TGA and DTA.

INTRODUCTION

Acylthiohydrazides

An important class of compounds, containing sulphur as an essential constituent, obtained by the action of hydrazine hydrate on carboxymethyl dithioate, is known as acylthiohydrazides. Thiohydrazides consist of $-CSNHNH_2$ group attached to an aromatic or heterocyclic nucleus. They may be represented by the formula:



(Where R= Phenyl, P- anisidyl, furfuryl and O-hydroxyphenyl etc.)

These compounds exist in two tautomeric forms.



Alongwith the donor capability of sulphur it has been shown that its presence in the compounds increases their therapeutic value. Further, the inclusion of a mercapto group (-SH) in a number of compounds has been found to increase the therapeutic value. The first compound to be examined for biological activity, 2- formylpyridine thiosemicarbazone, was shown to possess mild antileukemic activity against L-1210 tumour in mice at levels of drug which produced significant toxicity⁽¹⁾. The biological activity of such type of compounds is associated with chelation and direct correlation between anti-tumour activity and chelating ability of several such compounds was known. Also the increasing commercial value of transition metal complexes with sulphur donor ligands has created much interest in the field of Chemistry. A large number of hydrazides and hydrazones (Sasaki and Freiser, 1983) have shown significant amoebicidal activities. Salicylic acid hydrazide is particularly important due to its antituberculous (Notenboom et al., 1973) antipyretic, fungistatic and diuretic (Perkins et al., 1990) activities. Thus there has been considerable interest in the Chemistry of acid hydrazides and hydrazones because of their use in biological systems (Bhirud and Srivastava, 1990, Alcock et al., 1972, Katyal and Datt, 1975). The increased biological significance of sulphur compounds as well as of hydrazides promoted us to study the coordination capability of acyl thiohydrazides, as chelation with metal ions has been suggested one of the important mechanism for drug action

Coordination Capability of Acyl Thiohydrazides

This class of compounds necessarily consists of two nitrogen atoms and one sulphur atom. In addition of these, they may contain some other atom as well having free lone pair of electrons (like oxygen in the case of hydroxy acylthiohydrazide and therefore they exhibit the electron donor property. Thus they must act as versatile coordinating agents. The complexing properties of acylthiohydrazides and thiohydrazone derivatives have not been studied in much detail though a number of Ni(II) chelates have been reported (Gabel et al., 1977, Hansen and Larsen, 1977). Complexes of Ni(II), Pb(II), Co(II) and Co(III), Cu(II), Zn(II), Cd(II), Pb(II) and Hg(II) with O– hydroxyphenyl thiohydrazide have been reported by Keshari and Mishra (1981). These complexes have been characterized on the basis of UV, IR, electrical conductance and magnetic susceptibility measurements. Studies on the Ternary Complexes of Cu(II), Ni(II) and Co(II) with 3–indolyl thiohydrazide as primary ligand and picolinic acid or Quinoline – 2 – carboxylic acid as co–ligand have been carried out by Agarwal and Kumar. Some specific structural requirements are essential for complexation to occur and these requirements are fully satisfied in acylthiohydrazides.

Sulphur containing compounds are found to be most effective radioprotective agents in vitro and vivo. The mode of action of these compounds in modifying the radiation effects is generally thought to be a combination of the following processes : (i) Scavenging of potentially damaging primary water radicals and (ii) repair of damaged molecules by transfer of a hydrogen atom from the SH group. The reaction between oxygen containing radicals and certain thiols of biological interest such as glutathione and cysteine has been studied as one way of obtaining information about protection against oxidative stress (Rao et al., 1990). Such a process is often referred to as thiol pumping and the key step is believed to be the transformation of thiol function into a transient disulphide radical anion (RSSR⁻).

Maurya et al. (Rajnish et al., 1999, Ram et al., 1999, Maurya et al., 1997) have recently reported the synthesis and characterization of several cyanonitrosyl derivatives of chromium(I), manganese(I), vanadium(I) and molybdenum(O) by the interaction of appropriate cyanonitrosyl complexes of the respective metal ion with heterocyclic nitrogen and oxygen donors, and the aromatic amines, in hot aqueous–acetic acid media. Their results show that the partial replacement of the cyano groups by the reacting ligand takes place.

A few complexes of N–salicyloyl–N'–thiobenzhydrazide with trivalent metal ions have been isolated and characterized by elemental analysis, magnetic susceptibility measurements, UV–visible, IR and NMR–studies. The ligand and its complexes have shown remarkable in vitro anti-tumour activity against P–815 (murinemastocytoma) tumour cells.

Mixed ligand complexes of transition metals involving schiff bases have found application towards understanding of many reactions in living processes. In past such complexes have been studied as model complexes (De and Bhar, 1994) of biological importance. Mixed ligand complexes of cobalt(III) involving schiff bases have been studied in detail. The role of mixed ligand complexes in biological process has been well recognized. The stabilities of mixed ligand chelates are of great importance in biological system as many metabolic and toxicological functions are dependent upon stability. Synthesis of meal complexes having unusual coordination number through a process of mixed ligation is widely known. Mixed ligand complexes are expected to provide valuable information on magnetic properties, electronic spectra, flexidentate behaviour of polydentate ligands and stereochemistry.

Object and Scope of Work

A perusal survey of literature revealed that no work seems to have been done on the mixed ligand complexes with acylthiohydrazides as primary and pyridine carboxylic acids as coligands. This encouraged us to carry out the study of these complexes and the present work is an attempt in this direction.

In the present work we have synthesized N-acetyl-pyridine-N'-2-thiophene-thiocarboxyhydrazide. It is used as primary ligands and pyridine carboxylic acid; picolinic acid, dipicolinic acid and nicotinic acid as coligands.

Planning of Work

In the present paper I synthesised the mixed ligand complexes of Co(II) using the acyl thiohydrazide as primary and pyridine carboxylic acids as coligands. Further some of the synthesized mixed complexes have been screened for their anti-bacterial and anti-fungicidal activity with a view to know their biological significance.

In the present work we have tried to correlate analytical, magnetic, spectral and thermal properties of the mixed ligand complexes and tried to proceed the work on following lines.

- **1.** Preparation and purification of 2–Thiophen thiocarboxyhydrazide.
- 2. Condensation of thiohydrazide with 2–Acetyl pyridine.

3. Synthesis and isolation of coordination compounds of acyl thiohydrazides with Co(II).

Isolation of complexes formed with the reaction of binary complexes and pyridine carboxylic acid.

4. Evaluation of the antibacterial and fungicidal activity of newly synthesized mixed complexes.

5. Characterisation and confirmation of structures of the synthesized complexes with modern techniques.

6. Measurement of magnetic susceptibility of the complexes to ascertain oxidation state of the metal.

7. Nature of bonding involved in the isolated complexes by IR and electronic/reflectance spectral studies.

8. Determination of the geometry of isolated coordination compounds and the evaluation of relevant ligand field parameters i.e. Racah's inter–electronic repulsion parameter (B), Cubic ligand field splitting parameter (10Dq), nephelauxetic ratio (β), Dt, Dq^z, DT and DQ.

9. Thermogravimetric and DTA studies of the isolated compounds as far as possible.

Ligands

Acylthiohydrazide



2-Thiophene Thiocarboxyhydrazide $(C_5H_6N_2S_2)$



N-Acetyl Pyridine-N'-2-Thiophene Thiocarboxyhydrazide ($\mathsf{C}_{12}\mathsf{H}_{11}\mathsf{N}_3\mathsf{S}_2)$

Co-ligands Pyridine Carboxylic Acids



Nicotinic Acid $(C_6H_5NO_2)$

Picolinic Acid (C₆H₅NO₂)

$$\begin{array}{c} H = 0 \\ 0 = C \\ \hline \\ N \\ \hline \\ \end{array} \begin{array}{c} 0 = H \\ \hline \\ C = 0 \\ \hline \\ \end{array}$$

Dipicolinic Acid (C₇H₅NO₄)

MATERIAL AND METHODS Preparation and characterisation of ligands 2–Thiophen Thiocarboxyhydrazide

It was prepared by heating together 2–thiophencarboxaldehyde (30gm) in 120 ml ethanol and 150 ml of ammonium polysulphide solution at 70°C for about two hours. On cooling and acidification with concentrated hydrochloric acid, the dithio acid separated as red oil. It was extracted in ether. The etheral solution was treated with N–NaOH and its pH–raised to 7, then 35 gm of chloro acetic acid was added. After neutralizing it with sodium carbonate, the solution kept overnight at room temperature, when dark coloured solution formed. It was acidified with concentrated hydrochloric acid. The carboxy methyl ester separated as oil which crystallized on cooling. It was filtered off and recrystallised from water, as orange red crystals.M.P.122°C.



Carboxy methyl dithioate was then converted into thiohydrazide following the method of Jensen and Pederson. M.P.156°C.



N-Acetyl Pyridine-N'-2-Thiophene Thiocarboxyhydrazide

This compound was prepared by reacting 2–acetyl pyridine (0.1 M) and 2–thiophene– thiocarboxyhydrazide (0.1 M) in 50 ml. By refluxing the solution for one and half hour on water bath and on cooling gave colourless solid, which was filtered and washed with water. The compound was recrystallised from hot ethanol.

[M.P. 160° C. Found : C–55.10 H–4.17 N –16.04; S–24.44 (C₁₂H₁₁N₃S₂) requires C–(55.17) H–(4.21) N – (16.09) S– (24.52)].



N– Acetyl Pyridine–N'–2–Thiophene Thiocarboxyhydrazide ($C_{12}H_{11}N_3S_2$)

Pyridine Carboxylic Acid

Picolinic acid, nicotinic acid and dipicolinic acid were procured from Aldrich Chemical Company Inc. U.S.A. and used as such without further purification for the synthesis of mixed ligand complexes.



$(C_7H_5NO_4)$

Characterization of Acyl Thiohydrazides

The acyl thiohydrazides have been characterized on the basis of elemental analysis, molecular weight determination and IR spectral studies. Analytical and physical data of the acyl thiohydrazides are recorded in Table-1.

		% Chemical Analysis						
c			Found (Calculated)		Moleculear	
Э. N	Compounds	C	Ц	N	c	М.	Wt. Found	Colour
IN.		C	П	IN	5	Pt.	(Calculated)	Coloui
1.	2–Thiophen Thiocarboxyhydrazide $(C_5H_6N_2S_2)$	37.12 (37.97)	3.48 (3.79)	17.53 (17.72)	39.85 (40.50)	156 °C	165(158)	Orange red Crystal
2.	N–acetyl Pyridine–N'– 2–Thiophene Thiocarboxy hydrazide (C ₁₂ H ₁₁ N ₃ S ₂)	55.10 (55.17)	4.17 (4.21)	16.04 (16.09)	24.44 (24.52)	160 °C	270(261)	Colour- less

Table 1. Analytical and Physical Data of Acylthiohydrazide.

IR Studies

IR spectra of the free thiohydrazides showed two bands at 1530–1500 and 1282–1305 cm⁻¹ (thioamide bands–I and –II), characteristic vibrations of thioamide group (Rao C N R and Venkataraghavan, 1962, Rao et al., 1968). All the thiohydrazides, under study, displayed uC=S vibration due to thiocarbonyl group (thioamide amide band–IV) at 810–840 cm⁻¹. A band located at ~1000 cm⁻¹ in the spectra of ligands may be due to uN–N. Three strong bands appeared in the spectra of thiohydrazides at 3240–3280 and 3180–3195 and 3140–3150 cm⁻¹ assignable to uNH modes. The first band may be assigned to NH stretching of the imino group while the other two bands may be attributed to uNH of the primary amino group (Donaldson et al., 1965). The NH₂ deformation vibration is found to exist in the spectra of ligands at 1600–1630 cm⁻¹.

Thiophen thiocarboxyhydrazide displays bands at ~3010 cm⁻¹ characteristic of aromatic C–H stretch. The sharp band found at 645 and 570 cm⁻¹ and medium bands seen at 495 and 470 cm⁻¹ in the far IR spectrum of 2–APTTH are characteristic of thiophen C=C out–of–plane bending and C–S–C inplane bending modes (Jag Mohan, 2002, Geary, 1971), respectively. Diagnostic IR spectral bands have been tabulated in Table-2 and Figure-1.

				υ(C=S)				C=C
SNo	Compounds	Thioamide	Band	Thioami	(N_N)	UNH	<u>δ/N</u> ⊔2)	out–of–
5110.	compounds	I	П	de Band	0(11-11)			Plane
				IV				bending
	2 This share	1520011	1205	1020S	1000	3265 Sh		1015.0
1	2–Thiophen Thiocarboxybyd	15305H	1305 m	825 m	1000 Sh	3190 Sh		1215 5
1.	razide				511	3140 Sh	1640 S	
	(C5H6N2S2)							
				1020 S		3275 Sh		
	N–acetyl	1540SH	1290	820 m	1010	3190 Sh		1210 S
2	Pyriaine-N -2-		m		Sn	3150 Sh		
2.	Thiophene					5150 511		
	Thiocarboxy							
	hydrazide							
	(C12H11N3S2)							

 Table 2. Diagnostatic IR Spectra Band (cm⁻¹) of Acyl Thiocarboxyhydrazides.

STRUCTURAL STUDIES on Co(II) MIXED LIGAND COMPLEXES

A number of thiosemicarbazones containing nitrogen heterocycles are well known for their carcinostatic activity, which by loss of protons from their tautomeric thiol forms, can act as potential tridentate ligands sequestering metal ions involved in carcinogenesis. Mixed ligand complexes of 5– methyl–thiocarbanyl pyrazole–3–carboxylic acid having ONS donor set and pyridine, picolines, bipyridyl, O–phenanthrolin with heavy metal ions have been characterized on the basis of elemental analysis and various physico chemical techniques. Magnetic moment and electronic spectra data indicate that majority of the nickel(II) complexes and the bipyridyl and O–phenanthroline adduct of cobalt(II) are octahedral in nature while the cobalt(II) complexes with water or monodentate heterocyclic base molecules as coligands are composed of both tetrahedral and octahedral varieties. The ammonia adduct of nickel(II) appears to be a mixture of paramagnetic octahedral and diamagnetic square–planar forms. IR data suggest diprotic (ONS) tridentate function of the primary ligand in its thiol form in all these mixed–ligand species.

MATERIALS AND METHODS

Picolinic acid, Nicotinic acid, dipicolinic acid were Fluka reagents while 1,10–phenanthroline was obtained from M/S Eastman Kodak Company. Metal salts $CoCl_2.6H_2O$; $Co(NO_3)_2.6H_2O$ and other chemicals were BDH–reagents of AR–grade. Dioxan was used after further purification and the weighed amounts of ligands were dissolved in Dioxan water medium. Solutions of metal salts prepared in aceton/Dioxan containing little water and were used after standardisation.

General Procedure for the Synthesis of Complexes

The binary systems under investigation contained the metal ion and primary ligand in (1:1) and (1:2) molar ratios while the ternary systems contained metal ion primary ligand and secondary ligand in 1:1:1 molar ratio. After adjusting the pH to 8.0 the whole content was refluxed for two hours on water bath to complete the reaction. On cooling complexes of different colours were obtained. They were subjected to chemical analysis to confirm the molecular formulae.

An ethanolic solution of hydrated cobalt(II) salt (0.01 mol in 30 ml) was alkaliluated with a few drops of sodium hydroxide (pH~9.0) was treated with ligand N–acetyl pyridine–N'–2–thiophen thiocarboxy hydrazide /picolinic acid/ nicotinic acid/ dipicolinic acid (0.025 mol) dissolved in the same solvent in (1:1) molar ratio.

The resulting solutions were refluxed for 2–3 hours on steam bath, change in colour takes place. From the resulting solution coloured products separated slowly. The products were filtered, washed with cold ethanol and dried in vacuum over anhydrous calcium chloride.

Monochloro (N–acetyl pyridine–N'–2–thiophen thiocarboxy hydrazide) Co(II) chloride monohydrate. $[Co(C_{12}H_{11}N_3S_2)Cl]Cl.H_2O;$

Monochloro (nicotinato) (N-acetyl pyridine–N'–2–thiophen thiocarboxyhydrazide) Co(II) dihydrate. $[Co(C_{12}H_{11}N_3S_2)(C_6H_4NO_2)CI]2H_2O;$

Monobromo (nicotinato) (N-acetyl pyridine–N'–2–thiophen thiocarboxy hydrazide) Co(II)dihydrate. $[Co(C_{12}H_{11}N_3S_2)(C_6H_4NO_2)Br]2H_2O$

Monoiodo (nicotinato) (N-acetyl pyridine-N'-2-thiophen thiocarboxy hydrazide) Co(II)dihydrate. $[Co(C_{12}H_{11}N_3S_2) (C_6H_4NO_2)I]2H_2O$

Dipicolinato (N-acetyl pyridine-N'-2-thiophen thiocarboxy hydrazide) Co(II) monohydrate. $[Co(C_{12}H_{11}N_3S_2)(C_7H_3NO_4)]H_2O$

Monoaquo (dipicolinato) (2–thiophen thiocarboxyhydrazide) Co(II). [$Co(C_5H_6N_2S_2)(C_7H_3NO_4)H_2O$]

RESULTS AND DISCUSSIONS

All the synthesised mixed ligand complexes are non-hygroscopic and stable at room temperature. They could be stored for a sufficient time without change in colour. The mixed complexes are insoluble in common organic solvents but soluble in acetonitrile and dimethyl formamide.

Analytical data indicate 1:1:1 (M:L:L') stoichiometric composition for the complexes. Electrolytic conductance data measured in 10^{-3} M acetonitrile solution of the complexes reveals 1:1 electrolytic nature of some complexes. The low values of electrolytic conductance of few of the complexes indicate their non–electrolytic behavior (Singh and Srivastava, 1992). Presence of chloride ion was confirmed by adding silver nitrate solution (white curdy precipitate) and on warming with copper wire and concentrated H₂SO₄ presence or absence of brown fumes showing the presence or absence of nitrate ions in these complexes.

		congan	u.								
CI		% Chemical Analysis									
JI No	Complex		Found (Calculated)								
NO.	Complex	С	н	N	S	Х	М				
1		35.01	3.08	9.84	15.50	17.09	13.98				
1.	$[CO(C_{12}\Pi_{11}\Pi_{3}S_{2})CI]CI.\Pi_{2}O$	(35.21)	(3.17)	(10.27)	(15.65)	(17.36)	(4.41)				
2	2. [Co(C ₁₂ H ₁₁ N ₃ S ₂)(C ₆ H ₄ NO ₂)Cl]2H ₂ O		3.66	10.78	12.35	6.84	11.33				
Ζ.			(3.70)	(10.90)	(12.46)	(6.91)	(1.47)				
2		38.30	3.21	9.97	11.12	13.98	10.44				
э.	$[CO(C_{12}\Pi_{11}\Pi_{3}S_{2})(C_{6}\Pi_{4}\Pi_{2}O_{2})BI]Z\Pi_{2}O$	(38.7)	(3.40)	(10.03)	(11.47)	(14.33)	(10.56)				
4		35.62	3.09	9.0	10.37	20.80	9.64				
4.	$[CO(C_{12}\Pi_{11}\Pi_{3}S_{2})(C_{6}\Pi_{4}\Pi_{2}O_{2})]$	(35.70)	(3.14)	(9.25)	(10.57)	(20.99)	(9.74)				
-		45.08	3.09	10.98	12.16		11.33				
э.	$[CO(C_{12}\Pi_{11}\Pi_{3}S_{2})(C_{7}\Pi_{3}\Pi_{3}\Pi_{4})]\Pi_{2}O$	(45.33)	(3.18)	(11.13)	(12.72)		(11.71)				
c		42.0	3.58	10.80	12.23	6.75	11.30				
0.	6. $[CO(C_5\Pi_6N_2S_2)(C_7H_3NO_4)H_2O]$		(3.70)	(10.90)	(12.46)	(6.91)	(11.47)				
7		42.20	2.88	13.80	12.65		11.59				
1.	$[CO(C_{12}\Pi_{11}\Pi_{3}G_{2})(C_{6}\Pi_{4}\Pi_{10}G_{2})\Pi_{03}]$	(42.86)	(2.97)	(13.89)	(12.70)		(11.69)				

Table 3. Analytical data of mixed ligand complexes of Co(II) with N–Acetyl–Pyridine–N'–2– Thiophen Thiocarboxyhydrazide as primary and Picolinic acid/Nicotinic acid/Dipicolinic acid as

X = CI, Br, I etc.

Table 4. Physical data of mixed ligand complexes of Co(II) with N–Acetyl–Pyridine–N'–2–Thiophen Thiocarboxyhydrazide as primary and Picolinic acid/Nicotinic acid/Dipicolinic acid as coligand.

			$\Delta_{\rm m}$ in	in Molecular Weight		
Complex	Colour	M.Pt (°C)	DMF (ohm ⁻ ¹ cm ²) (mol ⁻¹)	Found	Calculated	Electrolytic Nature
[Co(C ₁₂ H ₁₁ N ₃ S ₂)(C ₆ H ₄ NO ₂)Cl]2H ₂ O	Brown	273	20.34	533.4 2	513.43	Nonelectro lyte
[Co(C ₁₂ H ₁₁ N ₃ S ₂)Cl]Cl.H ₂ O	Dark Red	298	107.3	430.2 6	408.93	1:1 Electrolyte
$[Co(C_{12}H_{11}N_3S_2)(C_7H_3NO_4)]H_2O$	Brown	308	18.4	521.1 0	502.92	Nonelectro lyte
$[Co(C_{12}H_{11}N_3S_2)(C_6H_4NO_2)Br]2H_2O$	Blue	292	4.2	569.8 4	557.93	Nonelectro lyte
[Co(C ₁₂ H ₁₁ N ₃ S ₂)(C ₆ H ₄ NO ₂)I]2H ₂ O	Pink	160	15.12	612.7 5	604.93	Nonelectro lyte
$[Co(C_5H_6N_2S_2)(C_7H_3NO_4)H_2O]$	Pink	315	8.6	416.3 3	399.93	Nonelectro lyte

Complex	Temperature (°K)	$\chi_{\rm m} \times 10^{-6}$	$\chi_{\rm m} \times 10^{-6}$	μ _{eff} (B.M.)
		(CGS Units)	(CGS Units)	
$[Co(C_{12}H_{11}N_3S_2)(C_6H_4NO_2)CI]2H_2O$	300	163.23 X 10 ⁻⁶	37.0 X 10 ⁻⁶	0.28
$[Co(C_{12}H_{11}N_3S_2)CI]CI.H_2O$	300	145.09 X 10 ⁻⁶	47.6 X 10 ⁻⁶	0.32
$[Co(C_{12}H_{11}N_3S_2)(C_7H_3NO_4)]H_2O$	300	150.18 X 10 ⁻⁶	53.3 X 10 ⁻⁶	0.38
$[Co(C_{12}H_{11}N_{3}S_{2})(C_{6}H_{4}NO_{2})Br]2H_{2}O$	300	10449.69 X 10 ⁻⁶	10380.1 X 10 ⁻⁶	5.0
$[Co(C_{12}H_{11}N_3S_2)(C_6H_4NO_2)I]2H_2O$	300	10806.13 X 10 ⁻⁶	797.8 X 10 ⁻⁶	5.10
$[Co(C_5H_6N_2S_2)(C_7H_3NO_4)H_2O]$	300	10206.98 X 10 ⁻⁶	10133.5 X 10 ⁻⁶	4.94

Table 5. Magnetic Susceptibility Measurements on mixed ligand complexes of Co(II).

Table 6. Reflectance Spectral Bands, their assignments and ligand field parameters of Co(II) Complexes.

Complex	Obs (cm A	served Bands 1 ⁻¹) and Their ssignments	Dq (cm⁻¹)	B (cm⁻¹)	β	Dq Calculate d (cm ⁻¹)	υ ₂ /υ ₁	L.F.S.E (K cal/ mol)
	9000	$^{4}T_{1g}(F) \rightarrow ^{4}T_{2g}(F)$						
$H_2NO_4)]H_2O$	18300	$^{4}T_{1g}(F) \rightarrow ^{4}A_{2g}(F)$	900	1008	0.90	972	2.03	16.66
	24000	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$						
	9030	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$						
$[CO(C_{12}\Pi_{11}N_3S_2)](C_6$ $H_1NO_1)C[]2H_1O$	18600	${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$	903	986	0.88	989	2.05	16.95
	24124	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$				989		
	9380	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$						
$[CO(C_{12}H_{11}N_3S_2)(C_6)$	18536	${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$	938	986	0.880	981	1.97	16.82
	23978	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$						
	9285	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$						
$[CO(C_{12}H_{11}N_3S_2)(C_6)$	18112	${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$	928	973	0.868	965	1.95	16.63
114102/1321120	24577	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$						
	8400	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$						
	17300	${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$	840	1024	0.91	984	2.05	16.40
0.1120	20210	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$						
	8450	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$						
$[Co(C_5H_6N_2S_2)(C_7H_5)]$	17615	${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$	845	1010	0.99	996	2.08	14.48
3100470203	20360	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$	T _{1g} (P)					
	8695	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$						
$[U(U_{12}H_{11}N_3S_2)](U_6$ $H_1NO_1NO_1^1$	18030	${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$	869	1002	0.98	930	2.07	14.89
	21415	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$						

Magnetic Measurement

The high spin octahedral complexes have the magnetic moment in the range 4.50–5.20 BM whereas the tetrahedral complexes have magnetic moment usually in the range 4.10–4.80 BM.

They may have higher magnetic moment than spin-only value due to higher orbital contribution. The magnetic moments of the complexes show the presence of three unpaired electrons and suggest octahedral configuration.

Reflectance Spectral Studies

In octahedral Co(II) complexes, three transitions are possible. ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)(\upsilon_{1}), {}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)(\upsilon_{2})$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)(\upsilon_{3})$.

The magnetic moment values for Co(II) complexes are in the ranges expected for octahedral geometry. In the electronic spectra of these complexes, two bands are mainly observed at ~9000 cm⁻¹ and ~24000 cm⁻¹, assigned to υ_1 and υ_3 transitions, respectively, considering a O_h symmetry. Two shoulders ${}^{4}T_{1g}(F) \rightarrow {}^{2}T_{1g}$, ${}^{2}T_{2g}(\sim18000 \text{ cm}^{-1})$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ (19000 cm⁻¹) may be considered either due to the splitting of υ_3 , in many components or they may be because of appearance of υ_2 transitions⁽⁴²⁾.the ratio of $\upsilon_2/\upsilon_1(1.95-2.2)$ suggests the shoulders ~19000 cm⁻¹ as υ_2 transitions for these complexes.

IR–Spectra

>C=S-Group

Thioamide band–I and thioamide band–II are observed at 1530 and 1280 cm⁻¹ in the IR–absorption spectra of N–acetyl pyridine–N'–2–thiophen thiocarboxy hydrazide, show a positive shift of 25–35 cm⁻¹ in the spectra of all the metal complexes. This shows participation of thione sulphur in the bond formation.

υ (C=N)

In the ligands the band around 1620 cm⁻¹ is assigned to $\upsilon(C=N)$ (azomethine) vibrations. The ligands with one primary amino group is expected to show two bands in the region 3100–3400 cm⁻¹ due to $\upsilon_s(NH_2)$ and $\upsilon_{as}(NH_2)$ vibrations. The presence of a phenolic group in such compounds make it difficult to differentiate between υNH_2 and $\upsilon(OH)$ vibrations since both absorbs around 3200 cm⁻¹ has been attributed to a combination of $\upsilon(NH_2)+\upsilon(OH)$ vibrations.

In the complexes, the ν (C=N) ν (NH₂) vibrations have undergone a negative shift by 40–50 cm⁻¹ indicating the coordination of the azomethine and primary amino groups of the thiophene-2thiocarboxy hydrazide and N-acetyl-pyridine-N'-2-thiophen Thiocarboxyhydrazide⁽²²⁾. This view is further supported by the appearance of bands corresponding to $\nu(M-N)$ and $\nu(M-S)$ in the far IR region. The presence of bands at 1540, 1460,1320 and 810 cm⁻¹ in the IR–spectrum of thiohydrazide ligands suggests that it exists in thione form in the solid state. In the IR-spectra of the complexes bands assigned to (N-C-N), C=S and (NH-C=S) reduces in frequency showing the involvement of thione sulphur atom in chelation. If ligands take part in thiol form then bands –N–C–N, C=S and NH– C=S disappear and new bands for the azine (C=N–N=C) and (C–S) group appear, indicating chelation of the metal ion through azine nitrogen and the thiolo sulphur of the ligand (Singh and Tandon, 1980, Sushil et al., 1999). The Pk₁ value of N-acetyl-pyridine-N'-2-thiophen thiocarboxy hydrazide (B) is (6.65) and that of thiophene–2–thiocarboxy hydrazide (A)(4.36). In both the compounds, there is a NH group on the azomethine N-atom. In such cases, the electron density on azomethine Natom should be higher because of lone-pair availability on the adjacent N-atom. This is reflected in their Pk values which are high. However, there is a drastic change in the Pk values of the two compounds. In both of them, the substituents on the NH group are electron-withdrawing. The abnormally low Pk value of compound (A) could be rationalized by taking into account the electronic picture of the thione group,



For a thione group the cannonical form (b) is more contributing than (a). The π -bond between C and S is very weak as it is formed by the unequal overlap of 2P-orbital of the carbon atom and the 3P-orbital of sulphur atom. Hence, the dipolar cannonical form (b) is the major contributing structure. As such the thione carbon atom is more electron-deficient, and the lone-pair on the adjacent N-atom would be strongly withdrawn to carbon atom.

Four cannonical structures (1,2,3,4) for $-NH-C(=S)-NH_2$ part of the thiosemicarbazone can be written as



Of these, the possibility of (3) would be more likely than (4) as the electron flow from –NH is more probable because it is attached to the azomethine N–atom. Thus this phenomenon would decrease the electron density on the azomethine N–atom substantially and thereby reducing the strength of hydrogen bond, and hence, accounting for the lower Pk_1 value of compound (A). In case of compound (B), the –NH group is attached to electron–withdrawing phenyl ring but still the lone pair on the N–atom may increase the electron density on the azomethine N–atom to some extent as the phenyl ring is not so a powerful electron–withdrawing group like the thione group. Hence, the Pk_1 value of (B) is higher (6.65) than (A) (4.36).

This change in the position of thioamide bands (compared with ligand) is indicative of the participation of sulphur of the thioamide group in bond formation with the metal ion. The positive shifts in these bands in the complexes are due to coordination through sulphur which decrease the C=S bond order and increase the C–N bond order due to inductive effect.

 ν C=S vibration, characteristic of thiocarbonyl group, observed as a medium band at 825 cm⁻¹ in the spectrum of the thiocarboxyhydrazide, get shifted to a lower frequency band(785–800 cm⁻¹) in the spectra of complexes (Rajnish et al., 1999, Ram et al., 1999).

The band characteristic of NH_2 deformation vibration found at 1,600 cm⁻¹ in the spectrum of the thiocarboxyhydrazide, (Thiophen–2–carboxy hydrazide), gets shifted to higher frequency of this band is in accordance with the coordinated NH_2 group. The band noticed at 3260 cm⁻¹ due to NH group is located almost at the same position in the spectra of complexes, showing that the nitrogen of the imino group is not involved in bonding in the complexes.

C–C, C–N and ring stretching absorptions existing at $1600-1400 \text{ cm}^{-1}$ in the spectra of pyridine carboxylic acids are shifted to higher frequency bands (1640-1650vs, 1605-1610, $1485-1492 \text{ cm}^{-1}$) in the complexes is suggestive of the ionation of electrons from ring nitrogen to the metal. The appearance of bands at ~1590 and 1400 cm⁻¹ corresponding to antisymmetric and symmetric COO stretching show the chelation through the oxygen atom of the deprotonated carbonyl group.

Some non–ligand bands have been found in the far infrared region in the ranges 370–480, 500–515 and 325–345 cm⁻¹ assigned to $\upsilon(M-N)$, $\upsilon(M-O)$ and $\upsilon(M-S)$ vibrations respectively. A band at ~200 cm⁻¹ is also seen in the spectra of complexes which may be due to $\upsilon(M-Cl)$ vibration (Maurya et al., 1997).

The presence of water in complexes is indicated by a broad band around 3400 cm⁻¹ and some what weaker bands around 850 and 700 cm⁻¹ assigned to OH stretching, rocking and wagging vibrations respectively. The absence of v_3 band of ionic nitrate at about 1360 cm⁻¹ and the appearance of two sharp bands at 1515–1525 and 1278–1285 cm⁻¹ in the spectra of complexes showed the coordination of nitrato group. The bidentate behaviour of the nitrato group is revealed by the appearance of bands at $1025(v_2)$, $820(v_6)$ and $725(v_3/v_5)$ cm⁻¹ The difference (40 cm⁻¹) in combination bands (v_1 + v_4) further confirms bidentate behaviour of nitrato group (Nakamotto et al., 1986). The bands existing at ~3010 and 1600 cm⁻¹, characteristic of aromatic C–H stretch and C–C ring stretch in the spectrum of the ligand are present in the spectra of complexes almost at the same position showing their non–involvements in complexation process (Figure 2.1 and 2.2).

conganus.									
Thioa	amide	υC=S		C=0,C=N					
Ba	nds	Thioam		& Ring	U _{as} COO				
		ide	ide		Stretchin	and	υM-	υM-	υM-
I	11	Band	2	gs	U _{sym} COO	Ν	0	S	
		IV		(Py)					
				1646vs,	100				
1585s	122Em	707	162	1608,	1205	750	515	335	
h	1222111	/0/W	5	1490	1395	m	m	w	
				1640vs,	4505				
1570s	1240	700	163	1605,	1585,	465	505	345	
h	1340	790W	5	1490	1399	m	m	w	
				1645vs,	4500				
1560s	1225.00	705	163	1610,	1592,	475	515	340	
h	13250	785W	0	1492	1395	m	m	w	
				1648vs,	1500				
1570s	1220m	705.0	164	1605,	1586,	480	510	325	
h	133011	795W	0	1485	1400	m	m	m	
				1650vs,	1505				
1565s	1220.00	700	163	1610,	1595,	460	500	340	
h	1338Ш	790W	3	1490	1405	m	m	m	
				1645vs,	1500				
1575s	1220m	800.0	162	1605,	1400	450	545	330	
h	1220111	800W	5	1490	1400	m	m	m	
	Thioa Ba I 1585s h 1570s h 1560s h 1570s h 1565s h 1565s h	Thioamide Bands I II I II 1585s 1335m 1570s 1340 1560s 1325m 1570s 1330m 1565s 1338m 1565s 1330m	Thioamide UC=S Thioamide UC=S Thioam ide Band Ide Ide	Thioamide Bands UC=S Thioam ide Band IV ANH 2 I II Band IV 100 1585s h 1335m 787w 162 5 1570s h 1340 790w 163 5 1560s h 1325m 785w 163 0 1570s h 1330m 795w 164 0 1565s h 1338m 790w 163 3 1575s h 1330m 800w 162 5	Thioamide Bands UC=S Thioam ide ANH ANH C=O,C=N & Ring Stretchin I II Band 2 & Ring Stretchin I II Band 2 gs (Py) 1585s 1335m 787w 162 1646vs, 1585s 1335m 787w 162 1640vs, 1570s 1340 790w 163 1605, 1560s 1325m 785w 163 1610, 1570s 1330m 795w 164 1605, 1570s 1330m 795w 164 1605, 1565s 1338m 790w 163 1610, 1565s 1338m 790w 163 1610, 1565s 1338m 790w 163 1610, 1575s 1330m 790w 163 1645vs, 1575s 1330m 790w 163 1645vs, 1575s 1330m 790w 163 1645vs, 1575s 1330m	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	

Table 7. IR Absorption bands(cm ⁻¹) in mixed ligand complexes of Co(II) with N-Acetyl Pyridine-N'-2-
Thiophene Thiocarboxyhydrazide as primary ligand and Picolinic/Nicotinic acid/Dipicolinic acid as

Thermal Behaviour

The elucidation of structure of the mixed ligand complexes are further established on the basis of thermal behaviour.

Cobalt complexes start loosing weight at 160-170°C with the loss of water molecule. This observation is in accordance with the presence of coordinated water in these complexes which is further confirmed by the appearance of bands characteristic of water in their IR spectra. The horizontal line on TG curve upto 190°C in the case of complexes shows their stability upto this temperature. All the complexes show decomposition abruptly in pure oxygen atmosphere in the temperature range 190–240°C. Pyridine carboxylic acid is completely removed from the complexes at this temperature range. NO₂ and O₂ gases also escape out in case of $[Co(C_{12}H_{11}N_3S_2)(C_6H_4NO_2)NO_3]$ Sharp exothermic peaks observed in the range 300-380°C in the DTA curve in conjunction with sudden mass loss at about 360°C in the TG curves correspond to the removal of half of Thiocarboxyhydrazide entity. Thereafter, a continuous mass loss is observed upto 500°C and organic part of the complex is completely eliminated at this temperature is seen in the TG curves. Practically at ~510°C a metallic oxide residue is obtained in each case. The TG curves acquire a permanent arrest beyond this temperature. But above 500°C, increase in the mass of the residue is observed upto 750°C and again a stable arrest is seen in the TG curves. At 750°C the weight of the residue corresponds to the formation of Co_3O_4 . The increase in the mass is probably due to the air oxidation of CoO into Co_3O_4 as observed by Sceney et al (2002). The decomposition products of the complexes are shown by the following flow sheets: (Figure 3.1 and 3.2).



$[Co(C_{12}H_{11}N_3S_2)(C_7H_3NO_4)]H_2O$

↓ 160-170°C

$\frac{[Co(C_{12}H_{11}N_{3}S_{2})(C_{7}H_{3}NO_{4})]}{\sqrt{210-240^{\circ}C}}$

Co(C₁₂H₁₁N₃S₂) ↓ 330–360°C

$Co(C_{12}H_{11}N_3S_2)_{1/2}$

↓ 510°C

CoO

↓ 750°C

Co_3O_4

$[Co(C_{12}H_{11}N_3S_2)(C_6H_4NO_2)Br]2H_2O$

↓ 190-220°C

[Co(C₁₂H₁₁N₃S₂)] ↓ 320°C-360°C

$[Co(C_{12}H_{11}N_{3}S_{2})_{1/2}] \\ \downarrow 510^{\circ}C$

CoO

↓ 750°C

Co_3O_4

$[Co(C_{12}H_{11}N_3S_2)(C_6H_4NO_2)I]2H_2O$

↓ 190–240°C

$Co(C_{12}H_{11}N_3S_2)$ \downarrow 310–360°C

Co(C₁₂H₁₁N₃S₂)_{1/2}

↓ 510°C

CoO

↓ 750°C

Co_3O_4

$[Co(C_5H_6N_2S_2)(C_7H_3NO_4) H_2O] \\ \downarrow 160-170^{\circ}C$

$\frac{[Co(C_5H_6N_2S_2)(C_7H_3NO_4)]}{\sqrt{210-240^{\circ}C}}$

Co(C₅H₆N₂S₂) ↓ 340–360°C

$Co(C_5H_6N_2S_2)_{1/2}$

↓ 510°C

CoO ↓ 750°C

Co₃O₄

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	Initial	Т	GA		
Complex	Decomposi	Temp	% Loss	Coosies Fermad	
Complex	tion	(°C)	Found	Species Formed	DIA
	Temp. (°C)	(- <i>j</i>	(Calcd.)		Peaks
		190-	13.56	$[Co(C_{12}H_{11}N_3S_2)CI]$	Endo
$[Co(C_{12}H_{11}N_3S_2)CI]CI.H_2O$	190	220	(13.08)	$[Co(C_{12}H_{11}N_3S_2)_{1/2}]$	Exo
		310-	22.22	CoO	Exo
		360	(21.76)		
		515	82.75		
			(81.67)		
		190-	38.33	$[Co(C_{12}H_{11}N_3S_2)CI]$	Endo
$[Co(C_{12}H_{11}N_3S_2)(C_6H_4NO_2)CI]2H_2O$	190	230	(37.68)	$[Co(C_{12}H_{11}N_3S_2)_{1/2}CI]$	Exo
		310-	64.50	CoO	Exo
		350	(63.10)		
		510	86.78		
			(85.40)		
		160-	(3.98)	$[Co(C_{12}H_{11}N_3S_2)(C_7H)]$	Endo
$[Co(C_{12}H_{11}N_3S_2)(C_7H_3NO_4)]H_2O$	160	170	(3.57)	₃ NO ₄)]	Endo
		210-	37.12	$[Co(C_{12}H_{11}N_3S_2)]$	Exo
		240	(36.38)	$[Co(C_{12}H_{11}N_3S_2)_{1/2}]$	Exo
		330-	63.44	CoO	
		360	(62.33)		
		510	86.59		
			(85.10)		
		190-	42.98	$[Co(C_{12}H_{11}N_3S_2)]$	Endo
$[Co(C_{12}H_{11}N_{3}S_{2})(C_{6}H_{4}NO_{2})Br]2H_{2}O$	190	220	(42.65)	$[Co(C_{12}H_{11}N_3S_2)_{1/2}]$	Exo
		320-	68.04	CoO	Exo
		360	(66.04)		
		510	88.12		
			(86.57)		
		190-	48.21	$[Co(C_{12}H_{11}N_3S_2)]$	Endo
$[Co(C_{12}H_{11}N_{3}S_{2})(C_{6}H_{4}NO_{2})I]2H_{2}O$	190	240	(47.11)	$[Co(C_{12}H_{11}N_3S_2)_{1/2}]$	Exo
		310-	69.13	CoO	Exo
		360	(68.68)		
		510	88.16		
			(87.71)		
		160-	4.90	$[Co(C_5H_6N_2S_2)(C_7H_3)]$	Endo
$[Co(C_5H_6N_2S_2)(C_7H_3NO_4)H_2O]$	160	170	(4.50)	NO ₄)]	Endo
		210-	46.13	$[Co(C_5H_6N_2S_2)]$	Exo
		240	(45.75)	$[Co(C_5H_6N_2S_2)_{1/2}]$	Exo
		340-	66.85	CoO	
		360	(65.51)		
		510	82.23		
			(81.26)		

 Table 8. Thermogravimetric Measurements of Mixed Ligand Complexes of Co(II).

It is observed that the complexes, having dipicolinic acid as co-ligand are slightly more stable. The tentative structures of the mixed ligand complexes based on the foregoing studies are traced on the next pages (Figure-4).

Evaluation of Antibacterial Activity

Bio-chemical, pharmacological and medicinal utility of a number of coordination compounds has been discussed. The best known biological function of Cobalt is its intimate involvement in the coenzymes related to vitamin B_{12} which is synthesized by bacteria. Nickel has some undisclosed function in living organism which can activate a number of metals in vitro bound to ribonucleic acids. It is found in blood and possesses peculiar affinity for bone and skin and plays important role in pigmentation. In this paper, Co(II) mixed ligand complexes have been screened for their inhibitory effects against four organisms viz., S. Aureus, B. Megaterium, Bacillus cereus (gram positive) and E.Coli (gram negative) by cup plate method.

Method for Evaluation of Antibacterial Activity

The composition of the culture media was maintained as:

1. Peptone	10 g.
2. Beef Extract	3.5 g.
3. Agar–agar	3.0 %
4. Sodium Chloride	5.8 g.
5. Yeast Extract	1.8 g.
6. Sucrose	2.0 g.
7. Sterilized Water	1.0 lt.

The pH of the test media was maintained at about 7.2. The measured quantity of the culture of the test organism (0.5 ml) was added to each agar–agar tube heated at $50-55^{\circ}$ C. After thorough shaking of the tube, inoculated media as favoured on the petri dishes and then kept for setting in a refrigerator. The test solutions of 0.05 m. concentration were prepared in the mixture of DMF and water (4:9). A number of cups were cut in the culture media on the petri dishes. The solution of the compound of known strength was put in the outer cups of the petri dishes. The central cups of all the petri dishes were filled with the controlled solution and all the petri dishes were kept in the refrigeration for about an hour. The petri dishes were transferred to an incubator maintained at $(35\pm1)^{\circ}$ C and kept for 30 hours. The zones of inhibition were measured and the activity results regarding the ligands and their complexes have been recorded in table-9.

Bacteria	APTTH	nicH	PicH	dipicH ₂	Co(APTTH)	Co(APTTH)	Co(APTTH)
					nic	pic	dipic
S.aureus	М	М	М	М	Н	Н	VH
B.megaterium	Р	М	Ρ	Р	М	Н	Н
B.cereus	М	М	М	Р	н	н	VH
E.coli	Р	Р	М	М	н	VH	н

P = poor, M = medium, H = high, VH = very high.

APTTH = N-Acetyl-Pyridine-N'-2-Thiophene Thiocarboxyhydrazide

The results of the evaluation of antibacterial activity show that all the synthesized complexes exhibit considerable activities towards all the four pathogenic bacteria. The activity of the mixed complexes is found to be greater than those of the metal salts and ligands.

Moreover, it has been noticed that the thiocarboxyhydrazide shows less activity towards E.Coli. The increased activity of the mixed ligand complexes may possibly be due to the combined activity effect of both the ligands present in the metal complexes or due to the reason that the complexes possess comparatively faster diffusion as a whole through the cells of the bacteria.

Fungicidal Activity

%

N-acetyl pyridine–N'–2–Thiophen Thiocarboxyhydrazide, pyridine carboxylic acids and the isolated Co(II) chelates were tested for fungicidal activity against Aspergillus niger, Fusarium oxysporum and Heliminthosphorium oryzae by the method described in the literature (Sceney et al., 1976). The experiments were carried out at $(27\pm1)^{\circ}$ C and 100 ppm in dioxan. Percentage was known by the following formula:

The results are tabulated in Table-10. The reported results show that the metal chelates are rather more active in comparison to the ligands. The reason of the increased activity is either the combined activity effect of the ligands or rapid diffusion of the metal chelate through the cells of fungi. The present chelates do not cause any change to the plants.

Table 10. Fungicidal Activity of Ligands and Co(II) Complexes.			
	% Inhibition After Five Days		
Compounds	Aspergillus	Fusarium	Heliminth
	niger	oxysporium	osporiumoryzae
(C ₁₂ H ₁₁ N ₃ S ₂)	64.0	18.2	78.2
$(C_6H_5NO_2)$ Picolinic Acid	48.3	40.0	59.8
(C ₆ H ₅ NO ₂) Nicotinic Acid	45.5	40.8	58.0
(C ₇ H ₅ NO ₄) Dipicolinic Acid	48.1	42.8	62.2
$[Cu(C_{12}H_{11}N_{3}S_{2})CI]CI.H_{2}O$	84.5	44.0	91.9
$[Cu(C_{12}H_{11}N_{3}S_{2})(C_{6}H_{4}NO_{2})CI]H_{2}O$	91.3	47.7	93.7
[Cu(C ₁₂ H ₁₁ N ₃ S ₂)(C ₇ H ₃ NO ₄)]H ₂ O	93.2	49.3	94.8
$[Cu(C_{12}H_{11}N_{3}S_{2})(C_{6}H_{4}NO_{2})NO_{3}]2H_{2}O$	84.0	52.3	91.1
$[Cu(C_{12}H_{11}N_3S_2)(C_6H_4NO_2)NO_3]$	92.1	52.7	93.8
$[Cu(C_5H_6N_2S_2)(C_7H_3NO_4)H_2O]$	94.2	55.8	95.9

Table 10. Fungicidal Activity of Ligands and Co(II) Complexes.



Fig. 1 : I.R. Spectra of Acylthiocarboxyhydrazide.



Fig. 2.1 : I.R. Spectra of Co(11) complexes.



Fig. 2.2: I.R. Spectra of Co(11) complexes.



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 $\label{eq:constraint} \begin{array}{l} \mbox{[Co(C_{12}H_{11}N_3S_2)(C_6H_4NO_2)Cl]2H_2O} \\ \mbox{Monochloro Nicotinato(N-Acetyl Pyridine-N'-2-Thiophene} \\ \mbox{Thiocarboxyhydrazide) Co(II) Dihydrate} \end{array}$



[Co(C₁₂H₁₁N₃S₂)Cl]Cl.H₂O Monochloro (N-Acetyl Pyridine-N'-2-Thiophene Thiocarboxyhydrazide) Co(II) Chloride Mono Hydrate



[Co(C₁₂H₁₁N₃S₂)(C₇H₃NO₄)]H₂O Dipicolinato (N-Acetyl Pyridine-N'-2-Thiophene Thiocarboxyhydrazide) Co(II) Mono Hydrate



[Co(C₁₂H₁₁N₃S₂)(C₆H₄NO₂)Br]2H₂O Monobromo Nicotinato (N-Acetyl Pyridine-N'-2-Thiophene

Thiocarboxyhydrazide) Co(II) Dihydrate



[Co(C₁₂H₁₁N₃S₂)(C₆H₄NO₂)I]2H₂O Monoiodo Nicotinato (N-Acetyl Pyridine-N'-2-Thiophene Thiocarboxyhydrazide) Co(II) Dihydrate



 $\label{eq:constraint} \begin{array}{l} [Co(C_5H_6N_2S_2)(C_7H_3NO_4)H_2O] \\ \mbox{Monoaquo Dipicolinato (2-Thiophene Thiocarboxyhydrazide) Co(II) } \end{array}$

Figure 4. Structures of the complexes prepared.

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REFERENCES

- Agrawal, K.C. and Sartorelli (1978). The chemistry and biological activity of alpha -(N)-heterocyclic carboxaldehyde thiosemicarbazones. *Prog. Med Chem* 15, 321-356.
- Sasaki, Y. and Freiser, H. (1983). Mixed-ligand chelate extraction of lanthanides with 1-phenyl-3methyl-4-acyl-5-pyrazolones, *Inorg Chem*, 22, 2289-2292.
- **Notenboom, H.R., Holland, W.J. and Soules, D. (1973).** Pyridine ketoximes as analytical reagents: The spectrophotometric determination of iron with 2,2'-dipyridyl-β-glyoximeMicrochimica Acta, 61 (1), 187-192.
- **Perkins, C.M., Rose, N.J. and Stenkamp, R.E. (1990).** The structure of cobalt methylmalonate complexes, CoClN4O7C10H28 and CoCl2N4O5.5C11H28, Models for metal complexes of γ-carboxyglutamic acid. *Inorganica Chimica Acta*, 172, 119-125, 172, 119-125.
- Bhirud, R.G. and Srivastava, T.S. (1990). Superoxide dismutase activity of Cu(II)2(aspirinate)4 and its adducts with nitrogen and oxygen donors, *Inorg Chim Acta*, 173, 121-125.
- Alcock, J.P., Baker, H.J. and Dimantis, A.A. (1972). The N-acylhydrazine grouping as a ligand. I. Coordination compounds of Keto- and Enol-N-acylhydrazines with cobalt(II), nickel(II), and copper(II), Aust. J. Chem. 25, 289-302.

Katyal, M. and Datt, Y. (1975). Analytical Analysis of hydrazones, Talanta, 22, 151.

- Gabel, J., Larsen, E. and Trinderup, P. (1977). Nickel(II) complexes of Thiohydrazonates.I, Acta Chem scand, 31 A, 657-665.
- Hansen, F. and Larsen, S. (1977). Nickel(II) Complexex of Thiohydrazonates. II. The Crystal and Molecular Structure of [Butanedione di(phenylacetthiohydrazonato)]nickel(II), Acta Chem. scand, 31A, 825-830.
- Keshari, B.N. and L.K. Mishra (1981). Thiohydrazides as Complexing Agents: Part I–Complexes of Ni(II), Pd(II), Co(II & III), Cu(II), Zn(II), Cd(II), Pb(II) & Hg(II) with o-Hydroxyphenylthiohydrazide, Indian J Chem, 20A, 883-887.
- Rao, D.N., Fischer, V. and Mason, R.P. (1990). Glutathione and ascorbate reduction of the acetaminophen radical formed by peroxidase. Detection of the glutathione disulfide radical anion and the ascorbyl radical *J Biol Chem*, 265, 844-847.
- Maurya, R.C., Mishra, D.D., Jaiswal, S.K. and Dubey, J. (1995). Synthesis, Magnetic and Spectral Studies of Some Novel Mixed-Ligand Cyanonitrosyl {MnNO}6 Complexes of Manganese(I) with Potentially Mono-, Biand Tri-Dentate Pyridine Derivatives synth react inorg met–org Chem, 25, 521-535.
- Maurya, R.C., Singh, H., Dubey, J. and Shukla, G.P. (1997). Metal Cyanonitrosyl Complexes: Synthesis, Magnetic, Thermal and Spectral Studies of Some Novel Mixed-Ligand Cyanonitrosyl {MnNO} Complexes of Manganese(I) with Potentially Mono – and Bidentate Aniline DerivativesSynth react inorg met–org Chem, 27 647.
- Maurya, R.C., Dubey, J. and Shukla, B. (1998). A Sincle-Step and Virtually Single Pot Synthesis of some Cynonitrosyl {Mn(NO) 2 } 7 Complexes of Manese(O) Involving 2/3-Pyrazoline-5-One Derivatives Directly from Manganate(VII), and Their Characterization, Synth react inorg metorg Chem, 28, 1159.
- **De, R.L. and Bhar, S.K. (1994).** Synthesis and characterisation of a new dinuclear cobalt(II) complex, Indian J Chem, 33A, 1034-1036.
- Rao, C.N.R and Venkataraghavan, R. (1962). The C=S stretching frequency and the "-N-C=S bands" in the infrared*Spectrochem. Acta., 18, 541-547.
- **Donaldson, J. D., Knifton, J.F. and Ross, S.D. (1965).** The effect of the lone pair on the infra-red spectra of some main group acetates Spectrochim. *Acta*, 21, 275-277.
- Jag Mohan (2002). Condensed hetrocyclic systems containing bridgehead nitrogen atom: Synthesis and antimicrobial activity of *s*-triazolo[3, 4-*b*] thiadiazines, thiazolo[3, 2-*b*]-*s*-triazoles and isomeric thiazolo[2, 3-*c*]-*s*-triazoles. Ind J. Chem, 41B, 403–406.
- **Geary, W.J. (1971).** The use of conductivity measurements in organic solvents for the characterisation of coordination compounds *Coord Chem Rev*, 7, 81-122.
- Singh, B. and Srivastava, A.K. (1992). Synthesis and structural studies of 2-acetylthiophene-2thenoylhydrazone complexes of oxovanadium(IV), manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and mercury(II), Proc Indian Acad Sci (Chem Sci), 104, 457-469.
- Singh, K., Singh, R.V. and Tandon, J.P. (1988). Coordination behaviour of biologically active benzothiazolines towards silicon(IV)Inorg *Chim Acta*, 151, 179-182.
- Singh, R.V. and Tandon, J.P. (1980). Semicarbazone & Thiosemicarbazone Derivatives of Silicon(IV), Indian J Chem, 19A, 602-604.
- Sushil K. Gupta, Kalpana Jain and Yogendra S. Kushwah (1999). Template synthesis and spectral speciation of nickel(II) macrocyclic complexes derived from 4-methyl-2, 6-di(formyl/benzoyl) phenol and diamines, Ind. J. Chem 38A, 506–508.
- Rajnish K. Sharma, Yash Pal Singh and Audhesh K. Rai (1999). Synthesis and structural elucidation of bis(N-/S-alkyl 2-aminocyclopentene-1-carbodithiato) diorganosilicon(IV), Ind. J Chem., 38A, 604–608.

- Ram C. Maurya, R. Verma and B. Shukla (1999). Coordination chemistry of dioxotungsten(VI) : Synthesis and characterization of some isothiocyanato complexes of dioxotungsten(VI) with biologically active chelating molecules, Indian Journal of Chemistry, 38A, 730–735.
- Maurya, R.C., Singh, T., Shukla, B. and Dubey, J. (1997). Metal Cyanonitrosyl Complexes: Synthesis and Characterization of Some Novel Mixed-Ligand Cyanonitrosyl {CoNO} 8 a Complexes of Co(I) with Some Biologically Active Heterocyclic Donors, Synth react inorg met–org Chem, 27, 1467.
- Nakamotto, K. (1986). Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th Edn. (John Wiley and Sons, New York), P 256.
- Jaya Gosain and Pradeep K. Sharma (2002). Kinetics and mechanism of the oxidation of formic and oxalic acids by tetrabutylammonium tribromideVol 41A, 321–324.
- Sceney, C.G., J.F. Smith, J.O. Hill and R.J. Magee (1976). J Thermal Anal, A TG/GC/MS Study of copper dimethyl-and Diethyldithiocarbamates, *J. Thermal Analysis*, 9, 415-423.

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