

Synthesis and Characterization of Mixed Ligand Complexes of Oxygen, Nitrogen and Sulphur Donor Ligands

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ABSTRACT: Synthesis mixed ligand complexes by the simple reaction of metal chloride, acetone semicarbazone and pyruvic acid thiosemicarbazone with having a formula $[M(ACSC)_1(PYTSC)_1(H_2O)_1]$. These synthesised complexes were characterized on the basis of elemental analyses, electronic, infrared, magnetic susceptibility, and also aid of molar conductivity measurement, thermal analysis, antimicrobial activities. Conductivity measurement reveals non electrolytic nature of the complex. On the basis of above analyses the octahedral structures are proposed for the prepared complex. The ligands are bonded through oxygen and nitrogen to metal ion.

KEYWORDS:- Mixed ligand complexes, semicarbazone, thiosemicarbazone, pyruvic acid acetone, thermal analysis, antimicrobial analysis.

I. INTRODUCTION

Coordination complexes have persist an important and popular area of research due to their simple synthesis, adaptability, and different range of applications. From the existing literature, it seems that transition metal complexes played a vital role in the development of coordination chemistry [1, 2]. It also plays an important role in biological process as exemplified in many instances in which enzymes are known to be activated by metal ions [3]. Coordination compounds display diverse characteristic properties which depend on the metal ion to which they are bound. On the basis of nature of the metal as well as the type of ligand, these metal complexes have wide applications in different fields of human curiosity [4, 5].

II. OBJECTIVES AND SCOPE OF THE PRESENT WORK

In this context, thiosemicarbazones are a class of compounds obtained by condensation of thiosemicarbazide with suitable aldehydes or ketones. In most complexes thiosemicarbazones behave as bidentate ligands because they can bond to metals through sulphur and the hydrazine nitrogen atoms, although pyruvic acid derivative of it acts as tri dentate ligand and bonding through sulphur, nitrogen and oxygen. Thiosemicarbazone derivatives are of special importance because of their versatile biological and pharmacological activities. Thiosemicarbazone derivatives have found application in drug development for the treatment of central nervous system disorders, of bacterial infection, as well as analgesic and ant allergic agent. Thiosemicarbazones are potent intermediates for the synthesis of pharmaceutical and bioactive materials and thus, they are used extensively in the field of medicinal chemistry. Moreover, thiosemicarbazones have found their way into almost every branch of chemistry; commercially they are used as dyes, photographic films, plastic and in textile industry. Over the years, thiosemicarbazone derivatives have demonstrated wide range of biological activity viz. Antimicrobial [5-10], antitumor [1-12], sodium channel blocker [13], anticancer [14-15], antitubercular [16], antiviral [17]. Keeping in mind various biomedical application of these class of compounds, we report the synthesis and characterization of mixed ligand complexes of acetone semicarbazone and pyruvic acid thiosemicarbazone with Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II).

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III. MATERIALS AND METHODS

The compounds pyruvic acid, acetone and semicarbazide hydrochloride and transition metal chlorides of Cr (III), Mn (II), Co (II), Ni(II) and Cu(II) used were of E MEARK, BDH, S D fine analytical grade.

The amount of metal is determined complexometrically by EDTA using suitable indicator. Carbon, hydrogen and nitrogen analyses were carried from SAIF, Mumbai and Central Research Laboratory, Pratap College, Amalner. Specific conductance were measured at room temperature in DMF by a Systronics direct reading 304 conductivity meter using a glass conductivity cell having a cell constant 1.0. IR and UV spectra were taken on JASCO 6600 FTIR SPECTROPHOTOMETER and JASCO - 670 -UV SPECTROPHOTOMETER from Central Research Laboratory, Pratap College, Amalner. Thermo gravimetric analyses were performed on STA 6000 from Department of Physics, Pratap College, Amalner. Microbial activities were carried out from PG Department of Microbiology, Pratap College, and Amalner.

Synthesis of Ligands: Ligands L1 and L2 were prepared. The methods of their preparation are given below.

Ligand: L1

PYRUVIC ACID THIOSEMICARBAZONE (PYTSC):

One mmole of pyruvic acid was added drop wise to the 20ml. methanolic solution of thiosemicarbazide (1mmole) with constant stirring. The reaction mixture was heated with reflux condenser for two hours. Then the reaction mixture is cooled to ambient temperature in a crushed ice. A light brown crystalline solid was formed. The product is filtered, washed and recrystallized from methanol, dried and melting point was recorded.

Ligand: L2

ACETONE SEMICARBAZONE (ACSC):

Dissolved 2 gm. of semicarbazide hydrochloride & 3 gm. of crystallized sodium acetate in about 25-30ml distilled water in a hard glass test tube to this solution add 2ml of acetone and shake well. Then cool this solution & transfer into a beaker containing crushed ice. White crystals of the semicarbazone derivative are separated out from the solution. Filter the crystals & recrystallized from ethyl alcohol, dry and then melting point and yield is recorded.

Synthesis Of complexes

1) Preparation of M (L1)₂ and M (L2)₂ complexes:

Aqueous 25 ml (0.01M) solution of metal chloride were mixed slowly with hot alcoholic 25 ml (0.02M) solution of the Pyruvic thiosemicarbazone (L1) with constant stirring. The reaction mixture is heated in water bath for three hours. Then the reaction was stirred for further one hour after which colored. Solid product was obtained, which was then washed with ethanol and dried in air. Similarly, the complexes of metals were prepared by mixing solution of corresponding metal chlorides and acetone semicarbazone ligand (L2) in 1:2 molar ratio respectively.

2) Preparation of mixed ligand complexes the type ML₁L₂:

The following general procedure was used to prepare the mixed ligand complexes of pyruvic acid thiosemicarbazone (PYTSC) and acetone semicarbazone (ACSC) with Cr(III), Fe(III), Mn(II), Co(II), Ni(II) and Cu(II).

To 20 ml ethanolic solution of 0.01M manganese chloride a mixture of 20 ml aqueous solution of 0.01M acetone semicarbazone and 20 ml 0.01M pyruvic acid semicarbazone ligands were added with continuous stirring in a water bath. Then the reaction mixture is refluxed with water condenser for half an hour. Then P^H of the reaction mixture was raised to 7.5 to 8.00 by adding 5% NaOH solution drop wise with constant stirring. The p^H was measured with the help of the p^H paper. Stirring was continued for another half an hour. The coloured precipitate of the complex separates out from the solution. The complex is filtered and dried under IR lamp. By using similar procedure other complexes were prepared by mixing metal salt solutions with pyruvic semicarbazone and acetone semicarbazone in the ratio 1:1:1.

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IV.RESULT AND DISCUSSION

A.ANALYTICAL PROPERTIES OF LIGANDS AND COMPLEXES

Physical properties of ligands are given in table I.

Table I:Physical properties of ligands.

Name of the ligand	Color and nature	Method of purification.	M.P. °c		Mol. wt	Molecular formula
			(observed)	reported		
Pyruvic acid Thiosemicarbazone	White shining crystals	Recrystallization from water	186	(186)	161	C ₄ H ₇ N ₃ O ₂ S
Acetone semicarbazone	White shining crystals	Recrystallization from CCl ₄	190	(188)	115	C ₄ H ₉ N ₃ O

The resulting complexes were having different colors as given in the table II. They are insoluble in chloroform, carbon tetrachloride, methanol, and ethanol but soluble in DMF. The properties of complexes are indicated in table II. The TLC of the mixed ligand complexes exhibit single spots with R_f values being intermediate of the two corresponding symmetrical bis-complexes indicating that these are mixed ligand complexes rather than a mixture of two corresponding bis-complexes. From the magnetic moments these complexes shows octahedral geometry.

The conductances of the complexes are very low (31.0-89.12Ω⁻¹cm²mol⁻¹) indicating their non-electrolyte nature.

The amount of metals present in complexes was determined volumetrically by EDTA using double burette technique for optimum utilization of reagents. Indicator ErichRome Black T was used for Cr(III) and Mn (II), ammonium thiocyanate for Fe (III), xylenol orange for Co(II) and mureoxide for Ni(II) and Cu(II) Carbon, hydrogen and nitrogen analysis were carried from SAIF, Mumbai AND Central Instrumentation Laboratory, Pratap College, Amalner.

Table II: Physical properties of complexes

Ligand/ Complex	Colour	Mole. wt	% Yield of The comp	% of metal (Calculated)	% of C	% of H	% of N	% of O	% of S
Cr[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	Gray green	452.49	72.01	11.47 (11.41)	18.56	3.53	18.56	10.59	7.03
Mn[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	Brown	420.93	65.03	13.07 (12.97)	19.95	3.80	19.95	11.20	7.60
Fe[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	Orange	456.35	73.24	12.23 (12.17)	18.40	3.50	18.40	10.50	7.00
Co[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	Dark green	423.93	71.02	13.90 (13.35)	19.81	3.77	19.81	11.31	7.54
Ni[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	Green	423.69	60.02	13.85 (13.74)	19.82	3.77	19.82	11.31	7.54
Cu[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	Green	428.54	64.21	14.82 (14.61)	19.60	3.73	19.60	11.19	7.46

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B. SPECTRAL PROPERTIES

ELECTRONIC SPECTRA

The electronic spectra of Cr(III) complexes exhibits bands in the range 11467, 22319 and 28089 cm^{-1} with ν_2/ν_1 ratio 1.946 corresponding to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (4G), ${}^6A_{1g} \rightarrow {}^4E_{2g}$ (4G), ${}^4A_{1g}$ (4G) and ${}^6A_{1g} \rightarrow {}^4E_{2g}$ (4D), transitions, respectively suggesting octahedral environment around Cr(III) ion. Mn(II) complexes shows bands in the range 12529, 21296 and 27032 cm^{-1} assignable to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G), ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (G) and ${}^6A_{1g} \rightarrow {}^4A_{1g}$ (G) transitions, respectively and magnetic moment indicates octahedral geometry. Co(II) complexes shows absorption bands 11428, 20986 and 24330 cm^{-1} with ν_2/ν_1 ratio 1.836, corresponding to ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (F), ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}$ (P) and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (F) transitions, respectively for octahedral geometry. The electronic spectra of Ni(II) complexes exhibits three bands in the range 10415, 19207 and 24603 cm^{-1} with ν_2/ν_1 ratio 1.844, corresponding to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively suggesting octahedral geometry. The six coordinated copper complexes shows bands in the range 11822, 18023 and 28079 cm^{-1} with ν_2/ν_1 ratio 1.5278 corresponding to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2E_{2g}$ transitions, respectively.

Table III: Electronic Spectra

Electronic spectral data of mixed ligand complexes of acetone semicarbazone and pyruvic acid semicarbazone.

Complex	Electronic Spectra		ν_2/ν_1	Stereochemistry
	$\lambda_{\text{max}}(\text{cm}^{-1})$	Assignment		
Cr[(PASC) ₁ (ACSC) ₁ (H ₂ O) ₁] Cl ₃	11467(sh)	${}^6A_{1g} \rightarrow {}^4T_{1g}$ (4G), ${}^6A_{1g} \rightarrow {}^4E_{2g}$ (4G)	1.946	Octahedral (Oh)
	22319(w s)	${}^4A_{2g} \rightarrow {}^4T_{2g}$		
	28089(w, s)	${}^4A_{2g} \rightarrow {}^4T_{1g}$		
Mn[(PASC) ₁ (ACSC) ₁ (H ₂ O) ₁] Cl ₂	12529 (m, br)	${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G),	1.697	Octahedral (Oh)
	21296(m, br)	${}^6A_{1g} \rightarrow {}^4T_{2g}$ (G)		
	27032(m,br)	${}^6A_{1g} \rightarrow {}^4A_{1g}$ (G)		
Fe[(PASC) ₁ (ACSC) ₁ (H ₂ O) ₁] Cl ₃	10438 (sh)	${}^6A_{1g} \rightarrow {}^4T_{1g}$ (t_{2g}) ⁴ (eg)	2.087	Octahedral (Oh)
	18094(m,br) 21786(m,br)	${}^6A_{1g} \rightarrow {}^4T_{2g}$ (F)(t_{2g}) ⁴ (eg)		
	29732(m,br)	${}^6A_{1g} \rightarrow {}^4E_g$, ${}^4A_{1g}$ (t_{2g}) ³ (eg) ²		
	31025(m,br)	${}^6A_{1g} \rightarrow {}^4T_{1g}$ (t_{2g}) ³ (eg) ²		
Co[(PASC) ₁ (ACSC) ₁ (H ₂ O) ₁] Cl ₂	11428(sh)	${}^4T_{1g} \rightarrow {}^4A_{2g}$ (F),	1.836	Octahedral (Oh)
	21786(sh)	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}$ (P)		
	24330(sh)	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (F)		
Ni[(PASC) ₁ (ACSC) ₁ (H ₂ O) ₁] Cl ₂	10417(w,br)	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$,	1.844	Octahedral (Oh)
	19207(w,br)	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$		
	24603(w,br)	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$		
Cu[(PASC) ₁ (ACSC) ₁ (H ₂ O) ₁] Cl ₂	11892(w,br)	${}^2B_{1g} \rightarrow {}^2A_{1g}$	1.527	Octahedral (Oh)
	18023(w,br)	${}^2B_{1g} \rightarrow {}^2B_{2g}$		
	28079(w,br)	${}^2B_{1g} \rightarrow {}^2E_{2g}$, Charge transfer		

IR SPECTRA

In the IR spectra of the mixed ligand complexes the bands at 1544-1604 cm^{-1} may be assigned to the symmetric and asymmetric $\nu(\text{C}=\text{N})$ vibrations. A strong band in the region 1748-1647 cm^{-1} are due to $\nu(\text{C}=\text{O})$ groups. On complex formation, the position of these bands is shifted toward lower side as compared to the metal free ligand. This indicates that the coordination takes place through the nitrogen and oxygen atom of the $(\text{C}=\text{N})$ and $(\text{C}=\text{O})$ groups. A broad band appears in the region at 3200-3750 cm^{-1} be attributed to the coordinated water molecule.

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Table IV. IR spectra (cm-1) bands of the parent and mixed ligand transition metal complexes

Ligand/Complex	ν_{OH} (H ₂ O)	ν_{OH} Carboxylic group	$\nu_{C=O}$	$\nu_{C=N}$	ν_{N-H}	ν_{C-N}	ν_{M-N}	ν_{M-O}	ν_{M-S}
Cr[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	3629	2356	1774	1615	1539	1044	875	724	481
Mn[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	3504	2349	1749	1621	1530	1113	862	743	487
Fe[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	3593	2343	1787	1615	1526	1104	869	739	467
Co[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	3589	2356	1795	1625	1519	1105	869	731	409
Ni[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	3551	2349	1747	1624	1523	1109	871	752	436
Cu[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	3519	2377	1715	1611	1520	1141	844	731	470

MAGNETIC PROPERTIES

The magnetic moment and electronic spectra of the complexes shows that the complexes have octahedral geometry. All the complexes are non electronic in nature.

Table V. Magnetic moment and molar conductance values of the complexes

Ligand/ Complex	Magnetic moment	Molar cond. $\Omega^{-1}cm^2mol^{-1}$ at room temp. (29°C)
Cr[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	4.01	31.40
Mn[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	5.623	51.70
Fe[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	5.085	50.23
Co[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	4.497	59.98
Ni[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	3.942	100.90
Cu[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	2.10	89.60

THERMAL ANALYSIS

The thermo grams (TG) of the compounds have been recorded in flowing nitrogen atmosphere at the heating rate of 10°C/min on approximately 10 mg samples Thermogravimetric analysis shows presence of one water molecules in the complexes supports the octahedral nature of complexes.

Table VI: Thermodynamic properties of complexes

Ligand/Complex	Temp. °C	% Mass Loss Found	DSC peak in °C Endo/Exo	ΔH in J g ⁻¹	ΔS^\ddagger	ΔG
Cr[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	50-200	4.485	219.33	-423.47	1.9307	-847.46
	201-300	46.383				
	301.458	11.83				
Mn[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	50-130	5.647	276.5	-667.44	2.413	-1334.88
	131-220	14.678				
	220-350	46.456				
Fe[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	50-150	6.476	460.37	-393.78	0.8553	-787.56
	150-300	37.45				
	300-428	29.45				
Co[(PATSC) ₁]	70-300	4.673	431.88	-839.03	1.9466	-1678.06

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(ACSC) ₁ (H ₂ O) ₁	300-467	18.35				
Ni[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	50-200 200-450	3.964 5.75	545.69	-826.16	1.5135	-1652.32
Cu[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	50-230 230-330 330-450	3.457 4.678 5.767	395.70	-280.28	0.2	-560.56

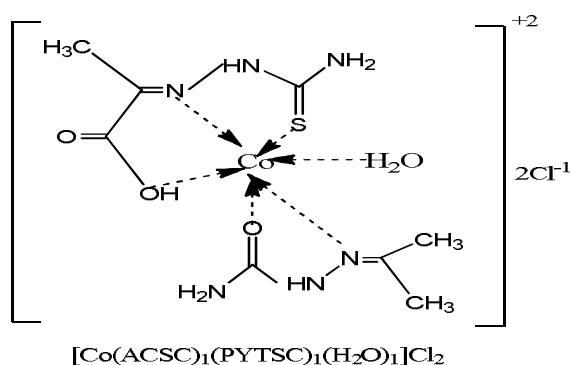
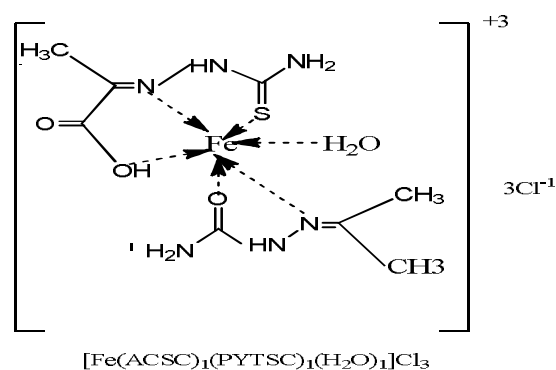
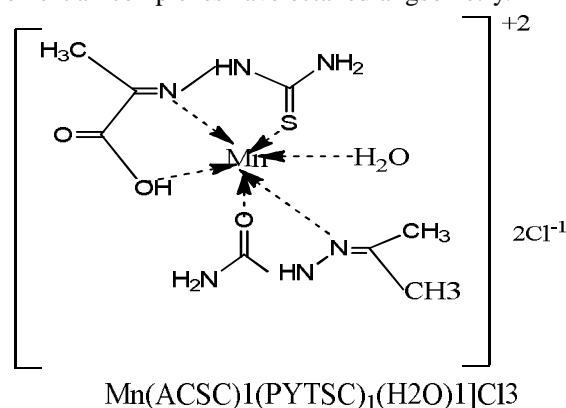
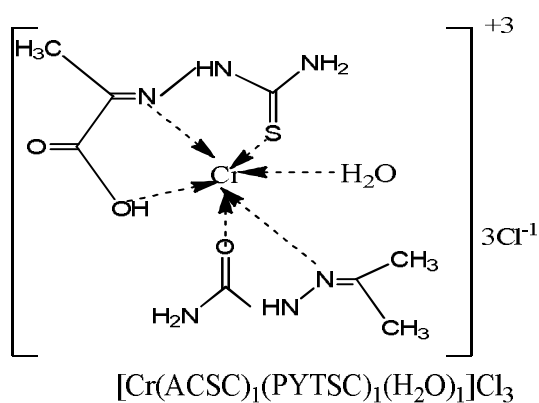
Biological Activities: The compound synthesized in the present investigation has been subjected to various antimicrobial screening programs based on their structural features so as to ascertain their activity against different microorganisms. The solvent used was DMSO.. The results of preliminary study on antimicrobial activity indicated that most of the compounds were highly and few were moderate active against these organisms.

Biological Activities of Ligands

Ligand/Complex	E.coli.	Baciullus Sp.	Staphylococ us.	Pseudomo nas Sp.	Proteus Sp.
Cr[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	8	11	12	6	10
Mn[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	8	8	9	10	11
Fe[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	9	10	9	9	11
Co[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	7	12	14	9	12
Ni[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	8	12	11	10	11
Cu[(PATSC) ₁ (ACSC) ₁ (H ₂ O) ₁]	10	15	13	14	12

Structure of the complexes:

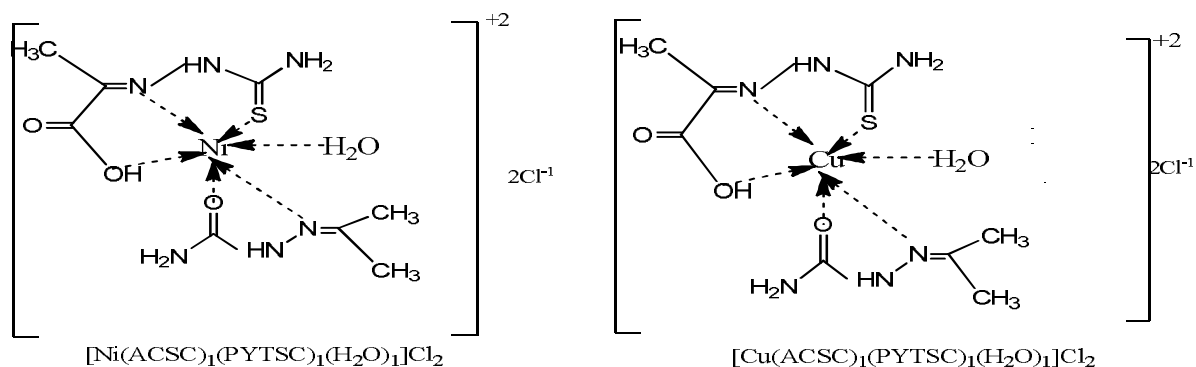
From all these analytical and spectrophotometric measurement all complexes have octahedral geometry.



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