



Research Article

STUDY OF MIXED LIGAND COMPLEXES OF ACETOPHENONE SEMICARBAZONE

Shirode,P.R*¹, Agrawal, R.K¹ and Yeole, P.M²

¹Department of Chemistry, Pratap College, Amalner

²Centre for P.G. Research in Chemistry, R.L. College, Parola, Dist. Jalgaon North Maharashtra University. Jalgaon (MAHARASHTRA)

ARTICLE INFO

Article History:

Received 9th November, 2016

Received in revised form 30th December, 2016

Accepted 24th January, 2017

Published online 28th February, 2017

Key words:

Mixed ligand, acetophenone , pyruvic acid, semicarbazone , transition metals.

ABSTRACT

The mixed ligand complexes of the type [ML₁L₂]Cl₂ have been synthesized, by the reactions of metal chlorides with two different ligands in 1:1:1 molar ratios. [Where M=Cr(III),Co(II), Ni(II) and Cu(II)] L₁=Pyruvic acid semicarbazone and L₂= Acetophenone semicarbazone. The resulting complexes have been characterized on the basis of elemental analysis, magnetic measurement, IR and Electronic spectra, conductivity measurement, thermal analysis, antimicrobial activities. The metal complexes show octahedral nature bonding through oxygen and nitrogen donor atoms.

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INTRODUCTION

Metal complexes have been receiving considerable attention for many years due to their interesting characteristics in the field of material science and biological systems. Optoelectronic, electrical and magnetic properties of the metals and metalloids can be tailored by reacting them with different ligands. A large number of Schiff bases and their complexes may exhibit the properties like- to reversibly bind oxygen, transfer of an amino group, as nano precursors and varied complexing/redox ability. The Schiff bases have high affinity to chelate with the transition metal ions, hence are attracting attention due to potential applications in areas viz. biology, catalysis, thermal, electrical, optical, magnetic etc [1-4]. A transition metal complexes which usually contain nitrogen, sulphur/or oxygen as ligand atoms are becoming increasingly important because these Schiff base can bind with different metal centers involving various coordination sites and allow successful synthesis of metallic complexes with interesting stereochemistry. Heterocyclic compounds are widely distributed in the nature and essential to many biochemicals, analytical and industrial processes. Compounds containing these heterocycles have important properties in the field of material science and biological systems [5-8]. The biological properties of semicarbazone are often related to metal ion coordination. In contrast to thiosemicarbazone, literature records fewer examples of semicarbazone presenting significant anticancer and cytotoxic activity but some nitro so, naphthopyran, and fluorine derivatives showed anti-leukemia effect in mice[9]. In this study we are reporting the synthesis and physicochemical characterization of Co(II), Ni(II) and Cu(II) complexes with ligands derived from

pyruvic acid semicarbazone and acetophenone semicarbazone.

Synthesis

The compounds pyruvic acid semicarbazone and acetophenone semicarbazone prepared and characterized in the laboratory for the synthesis of mixed ligand complexes with transition metal chlorides. The metal chlorides of Co(II), Ni(II) and Cu(II) used were of E MEARK ,BDH,S D fine analytical grade.

The following general procedure was used to prepare the mixed ligand complexes of pyruvic acid semicarbazone (PYSC) and acetophenone semicarbazone (ACPHSC) with Co(II), Ni(II) and Cu(II).

To 20 ml ethanolic solution of 0.01M. metal chloride a mixture of 20 ml alcoholic solution of 0.01M acetophenone semicarbazone and 20ml 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 two to three hours. If no solid product is obtained 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 colored precipitate of the complex separates out from the solution. In case of cobalt only 2-3 drops of NaOH is sufficient for to get the product. If more NaOH is added the colour of the complex darkens.

The complex is filtered and dried under IR lamp. By using similar procedure other complexes were prepared by mixing

metal salt solutions with Pyruvic acid semicarbazone and acetophenone semicarbazone in the ratio 1:1:1.

Analytical Properties

The resulting complexes were having different colors. They are insoluble in chloroform, carbon tetrachloride, methanol, ethanol but soluble in DMF. The properties of complexes are indicated in table 1. 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.

The amount of metals present in complexes were determined volumetrically by EDTA using double burette technique for optimum utilization of reagents. Indicator xylenol orange for Co(II) and Cr(III), mureoxide for Ni(II) and Cu(II). Carbon, hydrogen and nitrogen analysis were carried from Central Instrumentation 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 L₁ and L₂. IR spectra of the complexes were recorded on JASCO 6700 FTIR instrument using KBr pellets in the region 400-4000 cm⁻¹ from Department of Physics, Pratap College, Amalner and Central Instrumentation Laboratory, Pratap College, Amalner. Electronic spectra of complexes were recorded on JASCO -670 UV-VISIBLE Spectrophotometer in the Department of Chemistry, Pratap College, Amalner. Thermo gravimetric analysis was carried out on SHIMADZU STA 6000 from Department of Physics, Pratap College, Amalner.

Antimicrobial activities are determined in the PG department of Microbiology, Pratap College, Amalner by using three microbial nutrients.

Spectral Properties

Electronic Spectra

The electronic spectra of mixed ligand complexes of transition metals with pyruvic acid semicarbazone and acetophenone semicarbazone are shown in figures and the spectral data is represented in 2, 2a 2b.

Co(II) Complex

The reflectance spectrum of Co(II) complex is characteristic of Co(II) in octahedral environment, exhibiting three bands at 8271, 13755, 30211 cm⁻¹ with having transitions assigned for ⁴T_{1g}(F) ⁴T_{2g}(F), ⁴T_{1g} ⁴A_{2g} and ⁴T_{1g}(F) ⁴T_{1g}(P) respectively. Further support for the octahedral geometry is provided by the ratio λ₂/ λ₁ which is 1.643 indicating octahedral stereochemistry.

Ni(II) complex

The Ni(II) complex is high spin with a room temperature magnetic moment value of 3.57 B.M. This value is in the normal range observed for octahedral Ni (II) complexes. In addition, the complex displays three bands in the solid reflectance spectrum at 9532 cm⁻¹ for ³A_{2g} ³T_{2g}, 14792 cm⁻¹ for ³A_{2g} ³T_{2g}; cm⁻¹, and 32835 cm⁻¹ for ³A_{2g} ³T_{1g} (P) transitions. The spectrum shows a band at 34835 cm⁻¹ that may be attributed to L-M CT charge transfer. The 10Dq values 9532 cm⁻¹ confirm the octahedral configuration of the complex. The ratio λ₂/ λ₁ is expected to be in the range 1.5-1.7. The ratio is 1.551, which is near the expected range.

Table 1 Characterization data of the complexes

Ligand/Complex	Colour	Mol. For.	Mole. wt	% Yield of the comp.	% of metal calc. (obs.)	% of C	% of H	% of N
Co[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	Pink	CoC ₁₃ N ₆ O ₄ H ₁₁	469.93	63.01	12.54 (12.49)	33.19 (33.12)	4.04 (4.10)	17.87 (17.91)
Ni[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	Green	NiC ₁₃ N ₆ O ₄ H ₁₁	469.69	60.15	12.49 (12.39)	33.21 (33.15)	4.04 (4.03)	17.88 (17.81)
Cu[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	Pale green	CuC ₁₃ N ₆ O ₄ H ₁₁	474.54	53.65	13.38 (13.25)	33.71 (33.60)	4.00 (3.92)	17.70 (17.64)

Table 2 Electronic Spectra

Sr.no.	Name of the Complex	1	2	3	λ ₂ / λ ₁
1	Co[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	8271	13755	30211	1.643
2	Ni[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	9532	14792	32835	1.551
3	Cu[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	12919	26455	32286	2.047

Table 2a Electronic Spectra Electronic spectral data of mixed ligand complexes of pyruvic acid semicarbazone and acetophenone semicarbazone

Complex	Electronic Spectra	Stereochemistry
Co[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	λ _{max} (cm ⁻¹) 8271 13755 30211 Assignment ⁴ T _{1g} (F) ⁴ T _{2g} (F), ⁴ T _{1g} ⁴ A _{2g} , ⁴ T _{1g} (F) ⁴ T _{1g} (P)	Octahedral (Oh)
Ni[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	9532 14792 32835 ³ A _{2g} ³ T _{2g} , ³ A _{2g} ³ T _{2g} (P)	Octahedral (Oh)
Cu[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	12919 26455 32286 ² B _{1g} ² B _{2g} , ² B _{1g} ² E _g , ² B _{1g} ² A _{1g} .	Octahedral (Oh)

Table 2b Electronic spectral data and calculated transition energies (incm⁻¹) of the spin allowed bands in mixed ligand complexes of pyruvic acid semicarbazone and acetophenone semicarbazone.

Complex	Method of calculation	Obs.and cal. transition energies			B ₃₅	35	LFSE inKcal/mole	10Dq
		1	2	3				
Co[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]Cl ₃	Expt	8271	13755	30211			5.132	8554
	(a)	8281	14715	24908	969	0.9979	4.968	8281
	(b)	8915	15895	21268	923	0.9504	5.439	8915
	(c)	11992	17729	27189	743	0.7656	7.195	11992
[Ni(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]Cl ₂	(d)	8352	12649	28001	1239	1.276	5.010	8352
	Expt	9532	14792	32286			16.78	13986
	(a)	10Dq	27919	33534	600	0.5830	16.78	13986
	(b)	10Dq	21055	33789	999	0.9699	16.78	13986
	(c)	10Dq	21715	33910	859	0.8341	16.78	13986
	(d)	10Dq	20001	34843	1233	1.1980	16.78	13986

Cu(II) complex

The spectrum of Cu(II) complex consists of broad, low intensity shoulder bands centred at 12919 cm⁻¹ and 26455 cm⁻¹ and 32286 cm⁻¹. The ²E_g and ²T_{2g} states of the octahedral Cu(II) ion (d⁹) split under the influence of the tetragonal distortion that causes three transitions ²B_{1g}, ²B_{2g}, ²B_{1g}, ²E_g; and ²B_{1g}, ²A_{1g}. The magnetic moment of 2.01 B.M. falls within the range normally observed for octahedral Cu(II) complex.

IR Spectra

The infrared spectra of the synthesized complexes were recorded range 400-4000cm⁻¹, the important group frequencies of the (-OH of H₂O) (NH₂), (-OH of carboxylic group), (C=O), (C=N), (N-H), (C-N), (N-N), (M-N) and (M-O) vibration. Our investigation suggest that the ligand L₁-pyruvic acid semicarbazone and L₂-acetophenone semicarbazone coordinate with M (II)/M(III) forming Octahedral geometry.

For pyruvic acid semicarbazone bands observed at 3452 cm⁻¹, 2362 cm⁻¹, 1713 cm⁻¹, 1657 cm⁻¹, 1570 cm⁻¹, and 1157 cm⁻¹ are assigned for (-OH of carboxylic group), (C=O), (C=N), (N-H), (C-N), (N-N) groups, respectively. While acetophenone semicarbazone indicating bands at 3476cm⁻¹, 1749 cm⁻¹, 1671 cm⁻¹, 1558 cm⁻¹ and 1171 cm⁻¹ due to (NH₂), (C=O), (C=N), (N-H)(C-N) and (N-N), respectively.

On complex formation due to co-ordinate bond formation the frequency of group (-OH of carboxylic group) is lowered by 5-20 cm⁻¹, (C=O) by 4-24 cm⁻¹, (C=N) by 7-30 cm⁻¹ and (N-H) by 2-25 cm⁻¹. Another bands observed within the range 847-953 cm⁻¹ and 683-751 cm⁻¹ shows (M-O) and (M-N) bond formation. In addition, the band in the range 3557-3752 cm⁻¹ is assigned for the group (OH of H₂O) in the complexes, which is not observed in ligands.

IR spectral data is shown in table 3. **3.5. Magnetic Properties**
The magnetic moments, μ_{eff} of the complexes are given in table 3a and 3b

Table 3 IR spectra (cm-1) bands of the parent and mixed ligand transition metal complexes

Ligand/Complex	V _{OH} (H ₂ O)	V _{NH}	V _{OH of carboxylic acid}	V _(C=O)	V _{C=N}	V _{N-H}	V _{C-N}	V _{M-N}	V _{M-O}
PASC		3452	2362	1713	1657	1570	1157		
ACPHSC		3476		1749	1671	1558	1171		
Co[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	3723	3461	2339	1740	1633	1539	1148	855	683
Ni[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	3557	3459	2347	1721	1632	1533	1028	847	731
Cu[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	3752	3472	2354	1734	1653	1539	1156	943	737

Table 4 Magnetic moment and molar conductance values of the complexes Magnetic Susceptibility data of mixed ligand complexes of PASC and ACPHSC.

Complex	X _g in cgs units x 10 ⁻⁶	Mol.wt of complex	X _M in cgs units x 10 ⁻⁶	Pascal's correction 10 ⁻⁶	X _M x 10 ⁻⁶	μ _{eff} In B.M.
Co[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	12.86	469.93	6044.88	-197.93	6242.81	3.86
Ni[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	10.94	469.69	5142.14	-197.93	5340.07	3.57
Cu[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	3.15	474.54	1494.82	-197.93	1692.75	2.01

Table 4a Magnetic moment and molar conductance values of the complexes

Ligand/Complex	Magnetic moment	Molar cond. ¹ cm ² mol ¹ at room temp.(29 ⁰ C)
Co[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	3.86	64.24
Ni[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	3.57	59.53
Cu[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	2.01	48.76

Co(II) Complex

The Co(II) complex shows a magnetic moment of 3.86B.M. This value is in the range of octahedral geometry.

Ni(II) complex

For six coordinate Ni(II) complexes in a regular octahedral geometry consideration of spin-orbit coupling and contributions from ³A_{2g} and next higher ³T_{2g} state predicts the maximum value somewhat above the spin- only moment of 4.61 B.M. The magnetic moment of the complex is 3.57B.M. suggesting octahedral structure for this complex.

Cu(II) complex

The Cu(II) complex has a magnetic moment value of 2.01 B.M. Which supports octahedral character of the complex.

Electrical Conductivity

All the complexes are colored, non-hygroscopic and thermally stable solids (indicating a strong metal-ligand bond). The complexes are insoluble in water, ethanol, ethyl alcohol, acetone, chloroform, benzene but soluble in DMF and DMSO. The observed molar conductance values measured in DMF in 10⁻³M solution lie in the (48-81) ⁻¹cm²mol⁻¹ range, indicating their non- electrolytic nature are shown in table 4.

Biological Activities

The main objective of the synthesis of any antimicrobial compound is to inhibit the microbe without harming other biological cells. For in vitro antimicrobial activity, the metal complexes were tested against the bacteria. The MIC values of the compounds against the growth of microorganisms were summarised in the table 6. Complexation considerably reduces the polarity of the metal ions because of partial sharing of its positive charge with the donor group (the ligand), and also the electron density is delocalised due to the π back donation. Thus, the complexation process enhanced the lipophilic character of the central metal atom and hence liposolubility of the metal ion. In this way, the complexation favours the permeation of the metal ion through the lipid layers of the microorganisms' cell membrane. This permeation enhances the rate of uptake/access of the metal ion on the surface of the cell wall. These adsorbed metal ions disturb the respiratory process of the cells, thus blocking the synthesis of proteins, and in turn deactivates enzymes responsible for respiration processes. 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.

Table 5 Thermodynamic properties of complexes

Ligand/Complex	Temp. °C	% Mass Loss Found	DSC peak in °C Endo/Exo	H in J g ⁻¹	S [#]
Co[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	100-350	2.923	375.14	-897.032	1.3840
	350-400	8.632			
	400-800	3.842			
Ni[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	100-300	4.132	545.50	-826.143	1.0093
	300-800	2.142			
	100-150	2.142			
Cu[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	150-400	10.142	423.79	-280.2844	0.6613
	400-800	10.421			

Table 6 Biological Activities of Ligands and complexes

Ligand/Complex	E.coli.	Baciullus Sp.	Staphylococcus sp.	Pseudomonas Sp.	Proteus Sp.
Co[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	7	12	14	9	12
Ni[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	8	12	11	10	11
Cu[(PASC) ₁ (ACPHSC) ₁ (H ₂ O) ₁]	10	15	13	14	12

Thermogravimetric 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. The proposed decomposition stages, temperature ranges, decomposition products, and the calculated and found weight loss percentages of the complexes were presented in Table 5. In all investigated complexes, the first decomposition stage was the removal co-ordinated water molecule.

Thermogravimetric analysis of complex shows percentage loss of 3.634-5.437 in the temperature range 100-300°C. Which is attributed for loss of one water molecule in the complexes. which indicates the octahedral nature of complexes. Second stage is gradual decomposition of the complex.

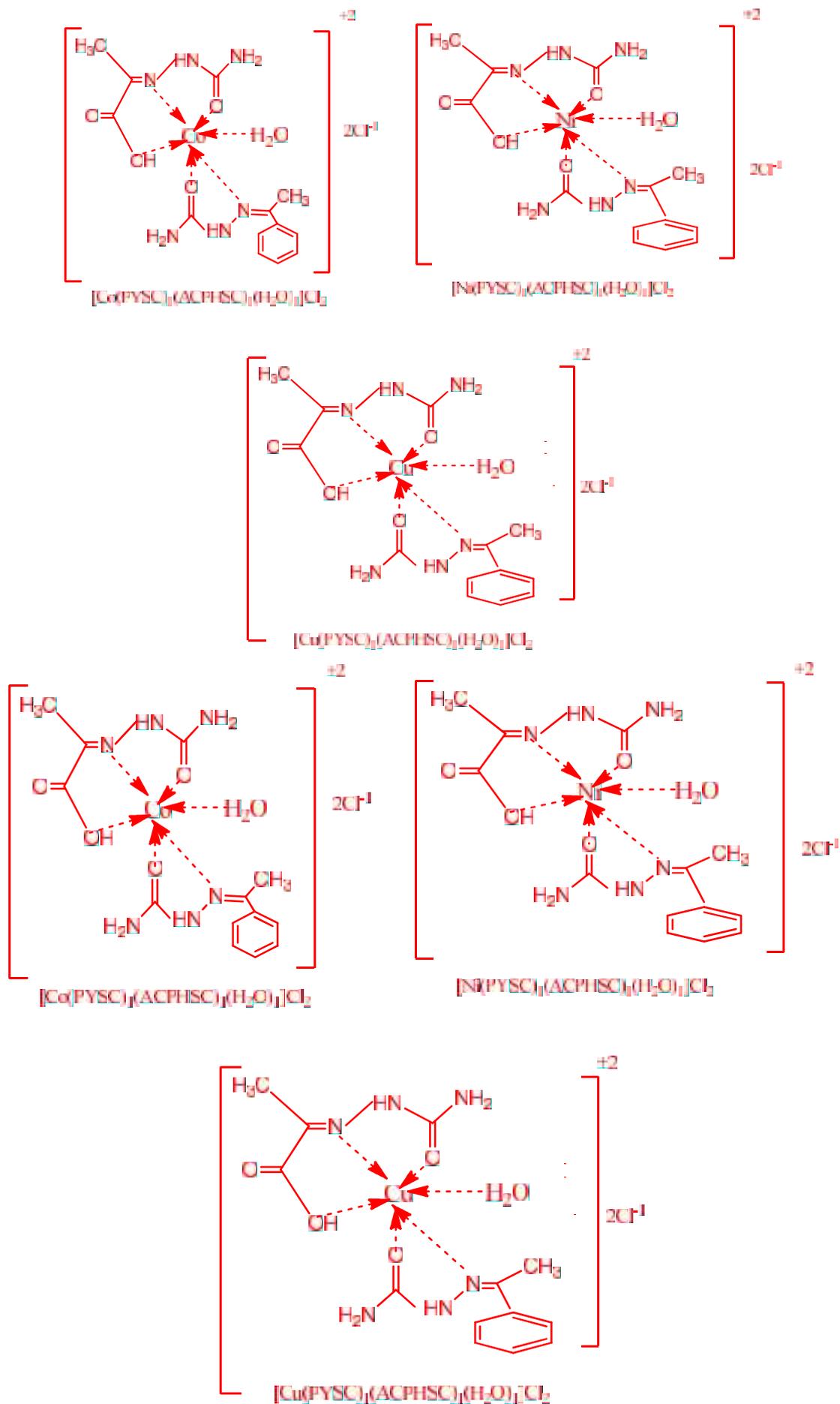
Complexes of Co(II), Ni(II) are more stable to heat as compared to complexes of other metals.

The solvent used was DMSO, and the sample concentrations were, 100ppm. The results of preliminary study on antimicrobial activity indicated that most of the compounds were highly and few were moderate active against these organisms. Microbiological activities of complexes are shown in table 6

Acknowledgement

I am grateful to Principal, Pratap college, Amalner Principal, R.L.College, Parola and Head, Department of Chemistry, Pratap College, Amalner for laboratory facilities. I am also thankful to the Head Physics Department Pratap College, Amalner for Electronic spectra and IR spectra and Head, SAIF, IIT Mumbai for elemental analysis

Structure of complexes



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