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A STUDY OF MIXED LIGAND COMPLEXES OF PYRUVIC ACID SEMICARBAZONE WITH TRANSITION METAL CHROMIUM(III)

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ABSTRACT

The mixed ligand complexes of the type $Cr(L_1L_2)Cl_2$ Where L_1=pyruvic acid semicarbazone and L_2= acetone semicarbazone, benzaldehyde semicarbazone, acetophenone semicarbazone, cyclohexanone semicarbazone have been synthesized by the reaction of chromium chloride with two ligands L_1 and L_2 in the ratio 1:1:1 molar ratio. The resulting complexes have been characterized on the basis of elemental analysis, magnetic measurement, IR and UV spectral analysis, conductivity measurement, thermal analysis, antimicrobial activities. Analysis of results reviles that the complexes shows octahedral geometry, electrolytic nature and having more antimicrobial activity than the ligands. The ligands are bonded through oxygen and nitrogen.

KEYWORDS: The mixed ligand benzaldehyde semicarbazone, oxygen and nitrogen.

INTRODUCTION

There has been growing interest in the formation of mixed ligand chelates involving ligands containing different functional groups and transition metals of different oxidation states. Transition metal complexes of pyruvic acid semicarbazone shows remarkable antitumor, antiviral, anticancer, anti-malarial, anti-fungal, anti-bacterial and catalytic activities. In view of these applications, we have carried out synthesis and characterization and biochemical study of mixed ligand complexes chromium(III) with pyruvic acid semicarbazone and L_2= acetone semicarbazone, benzaldehyde semicarbazone, acetophenone semicarbazone, cyclohexanone semicarbazone.

In this complexation reaction acetone semicarbazone, benzaldehyde semicarbazone, acetophenone semicarbazone, cyclohexanone semicarbazone. are acting as a bidentate ligands and pyruvic acid semicarbazone is acting as a tridentate ligand with oxygen and nitrogen as the donor species.

MATERIALS AND METHODS

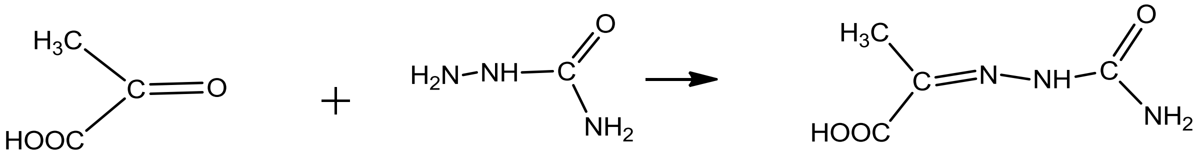
The compounds acetone, benzaldehyde, acetophenone, cyclohexanone, pyruvic acid, semicarbazide hydrochloride and chromium(III) chloride used were of analytical grade. The amount of metals are determined volumetrically by EDTA using double burette technique for optimum utilization of reagents. Indicator Eriochrome Black T is used Carbon, hydrogen and nitrogen analysis were carried from SAIF, Mumbai. IR spectra of the complexes were recorded on Perkin Elmer FTIR instrument using KBr pellets in the region 400-4000 cm-1 from Department of Physics, Pratap College, Amalner. Electronic spectra of complexes were recorded on Systronics UV-VISIBLE Spectrophotometer in the Department of Chemistry, Pratap College, Amalner. The IR spectral data of complexes is shown in table 3. Thermo gravimetric analysis was carried out on SHIMAdZU STA 6000.Antimicrobial activities are determined by using three microbial nutrients. Ligands L_1 and L_2 were prepared and the methods of their preparation are given below.

Ligand: L_1

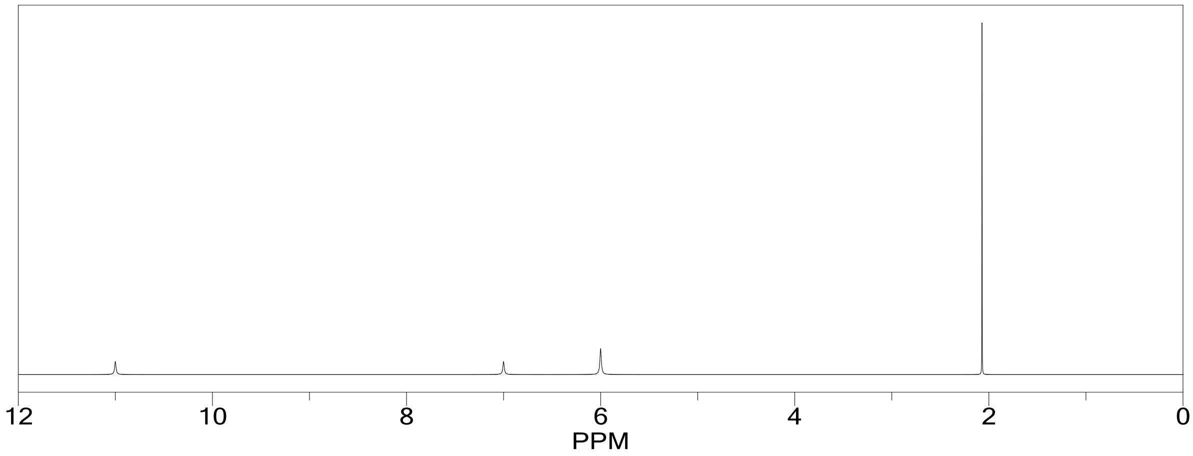
1. Pyruvic Acid Semicarbazone

Dissolve 2 gm. of Semicarbazone hydrochloride and 3 gm. of sodium acetate in a 100 ml beaker In 20-30 ml distilled water & stir continuously to obtained a clear solution of mixture of semicarbazide hydrochloride & sodium acetate, filter the solution & place ice bath. Take 2ml of pyruvic acid in a test tube and cool it in ice bath. This ice cooled solution of pyruvic acid is very slowly drop wise added in a ice cooled solution of mixture of sodium acetate and semicarbazide hydrochloride with constant stirring. Stir the reaction mixture for another half an hour to separate out white precipitate of pyruvic acid semicarbazone. Recrystallize the crude product from hot water, dry and then melting point and yield is recorded.

Reaction



NMR Spectrum

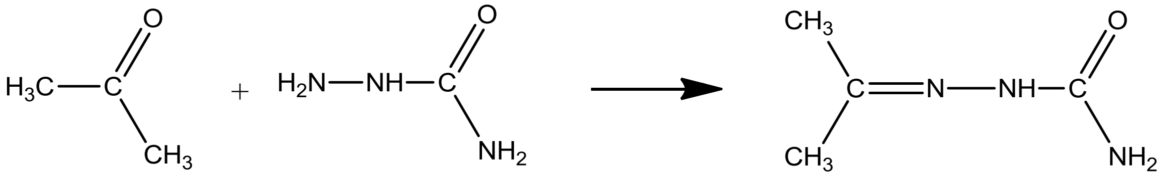


Ligand: L_2

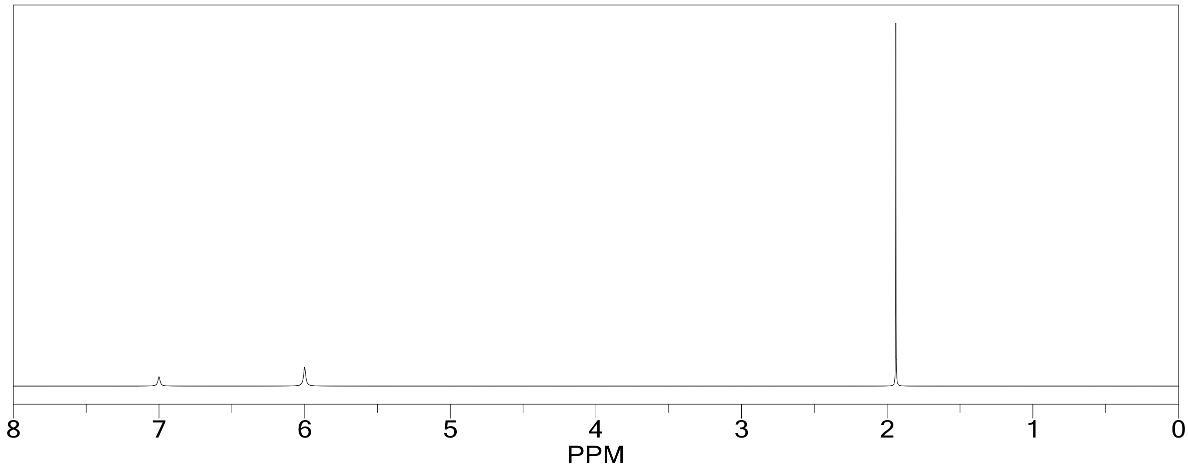
1. Acetone Semicarbazone

Dissolved 2 gm. of semicarbazide of hydrochloride & 3 gm. of crystallized sodium in about 25-30ml distilled water hard glass test tube, cool in ice bath, to this solution add 2ml of acetone drop by drop with constant stirring for half an hour. White crystals of the semicarbazone derivative are separate out from the solution. Filter the crystals & recrystallized from ethyl alcohol, dry and then melting point and yield is recorded.

Reaction

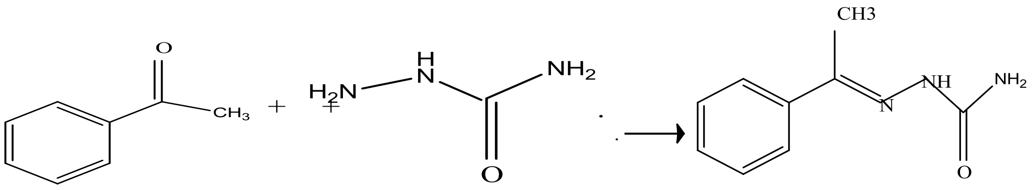


NMR spectrum

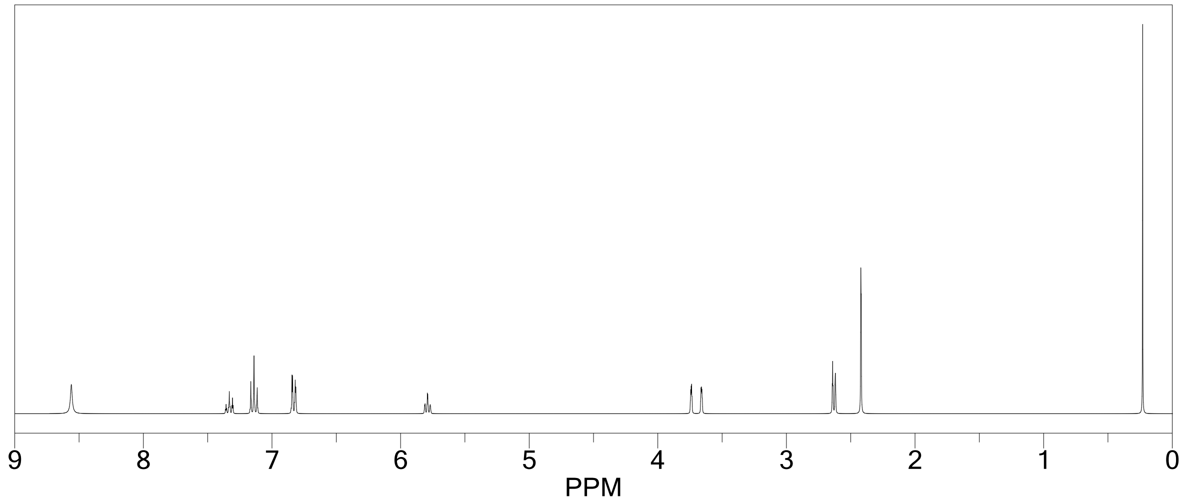


2. Acetophenone Semicarbazone

Dissolved 2 gm. of semicarbazide of hydrochloride & 3 gm. of crystallized sodium acetate in about 25-30ml distilled water in hard glass test tube to this solution add 1ml of acetophenone & shake well. If the mixture is turbid then add 1:1 ethyl alcohol until a clear solution is obtained. Than heat this reaction mixture in water bath for 10 mints. Than cool this solution & transfer into a beaker containing crashed ice. White crystals of the semicarbazone derivative are separate out from the solution. Filter the crystals & recrystallized from ethyl alcohol, dry and then melting point and yield is recorded.



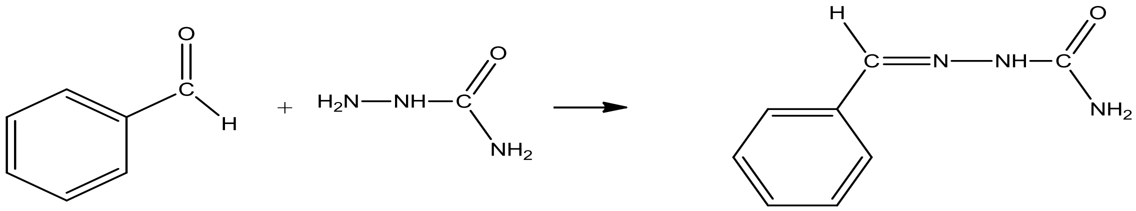
NMR Spectrum of acetophenone semicarbazone

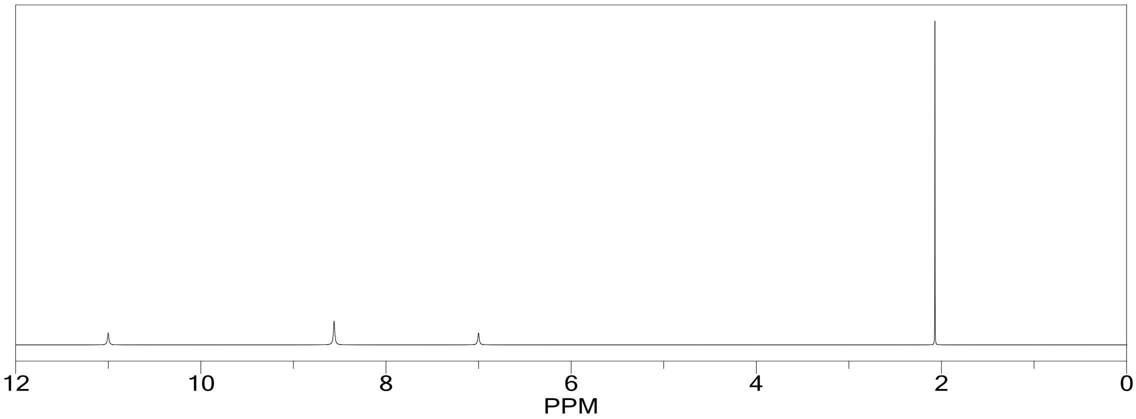


3. Benzaldehyde Semicarbazone

Dissolved 2 gm. of semicarbazide of hydrochloride & 3 gm. of crystallized sodium acetate in about 25-30ml distilled water in hard glass test tube to this solution add 1ml of benzaldehyde & shake well. If the mixture is turbid then add 1:1 ethyl alcohol until a clear solution is obtained. Than heat this reaction mixture in water bath for 10 mints. Than cool this solution & transfer into a beaker containing crashed ice. White crystals of the semicarbazone derivative are separate out from the solution. Filter the crystals & recrystallized from ethyl alcohol, dry and then melting point and yield is recorded.

Reaction

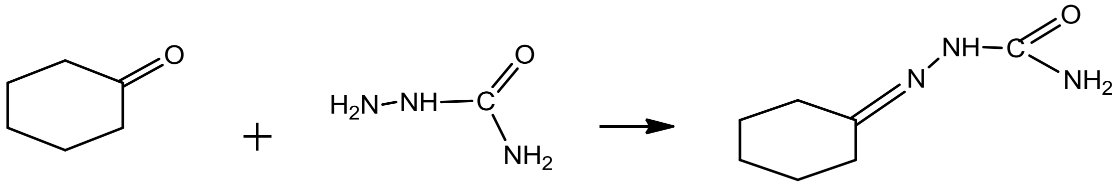




4. Cyclohexanone Semicarbazone

Dissolved 2 gm. of semicarbazide of hydrochloride & 3 gm. of crystallized sodium acetate in about 25-30ml distilled water in hard glass test tube to this solution add 1.3 ml of cyclohexanone & shake well. If the mixture is turbid then add 1:1 ethyl alcohol until a clear solution is obtained. Then heat this reaction mixture in water bath for 10 mints. Than cool this solution & transfer into a beaker containing crashed ice. White crystals of the semicarbazone derivative are separate out from the solution. Filter the crystals & recrystallize from ethyl alcohol, dry and then melting point and yield is recorded.

Reaction



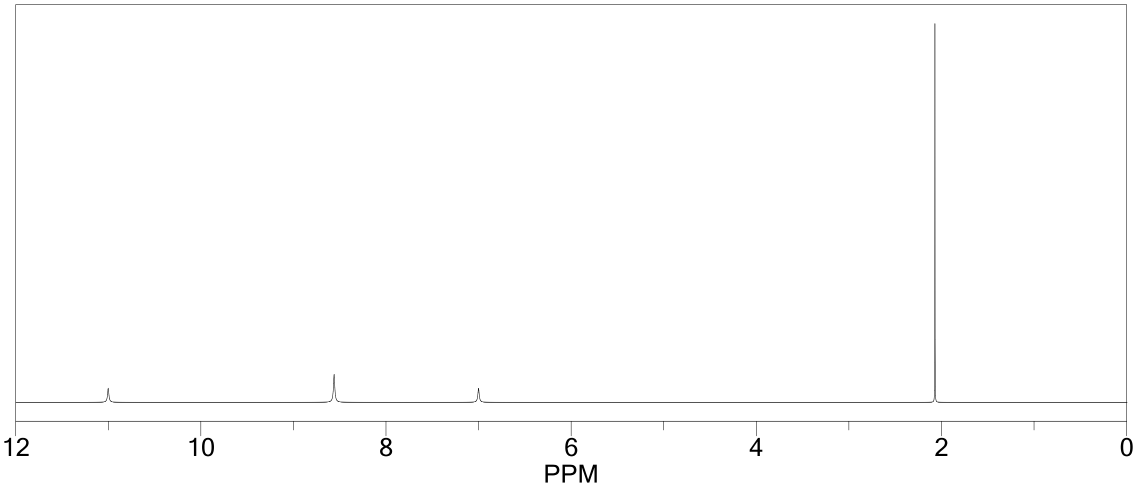


Table I: Physical properties of ligands.

Name of the ligand	Color and nature	Method of purification.	M.P. ^{0}c (observed)	reported	Mol. wt	Molecular formula
Pyruvic acid semicarbazone	White shining crystals	Recrystallization fromwater	215(214)	(214)	145	$C_4H_7N_3O_3$
Acetone semicarbazone	White shining crystals	Recrystallization from CCl_4	190(188)	(188)	115	$C_4H_9N_3O$
Acetophenone semicarbazone	White shining crystals	Recrystallization from ethanol	199	(200)	177	$C_9H_{12}N_3O$
Benzaldehyde semicarbazone	White shining crystals	Recrystallization from ethanol	222	(221)	163	$C_8H_9N_3O$
Cyclohexanone semicarbazone	White shining crystals	Recrystallization from ethanol	167	(167)	155	$C_7H_{13}N_3O$

Synthesis of transition metal complexes of the type $M(L_1)_2$

Aquous solution pyruvic acid semicarbazone was added to methanolic solution of chromium(III) chloride in 1:2 molar praporation with continuous stirring at room temp, till clear solution was obtained. Then the solution was refluxed on a heating mental at about 60-70^{0}C for four hours. The colored solid complex separates out from solution. The product was filtered on cooling, washed with methanol, dried under inert atmosphere and practical yield of complex is measured.

Synthesis of transition metal complexes of the type $M(L_2)_2$

This complex is prepared by mixing methanolic solution of metal chloride and alcoholic solution of ligand L_2 in the 1:2 molar preporation with continuous stirring at room temperature., The clear shown was refluxed on a heating mental. Then the solution was refluxed on a heating mental at about $60\text{-}70^0C$ for four hours. The colored solid complex separates out from solution. The solid product is filtered on cooling, washed with methanol, dried in inert atmosphere.

Synthesis of transition metal complexes of the type ML_1L_2

In a round bottom flask containing alcoholic solution of metal chloride, hot ethanolic solution of mixture of pyruvic acid semicarbazone and acetone semicarbazone in the molar preporation 1:1:1 was added with continuous stirring at room temp, till clear solution was obtained. Then the solution was refluxed on a water bath for four hours. The colored solid complex separates out from solution. The solid product is filtered on cooling, washed with methanol, dried and weight of the complex obtained is taken to determine practical yield.

Similarly, complexes of pyruvic acid semicarbazone with benzaldehyde semicarbazone, acetophenone semicarbazone and cyclohexanone with chromium chloride were prepared by mixing equimolar quantities in 1:1:1 proportions.

RESULTS AND DISCUSSION

Analytical Properties

The mixed ligand complexes formed were having different colors as shown in the table 2. These complexes were insoluble in chloroform, carbon tetrachloride, methanol, ethanol but soluble in DMF. The properties of complexes were indicated in table 2. The TLC of the mixed ligand complexes with $M(L_1)_2$ and $M(L_2)_2$ was taken. It exhibit single spot with R_f values being intermediate of the two corresponding symmetrical bis-complexes. From the magnetic moments these complexes shows octahedral geometry. The amount of metals present in complexes were determined volumetrically by EDTA using double burette technique for optimum utilization of reagents using Erichrome black T as an indicator. 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 L_1 and L_2. Antimicrobial activities were determined in the PG department of Microbiology, Pratap College, Amalner by using three microbial nutrients.

The elemental analysis shown in Table 2 indicates that, all the metal complexes have 1:1:1 stoichiometry and are, soluble only in DMF and DMSO. The molar conductance values obtained for these complexes at the concentration of 10^{-3} M are in the range of 52-109 ohm^{-1} mol^{-1} cm^{2}. The magnetic moments these mixed ligand complexes shows that these complexes were having octahedral geometry.

Table 2.

Ligand/ Complex	Colour	Mole. wt	% Yield of the comp.	% of metal (Calculated)	% of C	% of H	% of N	% of O
[Cr (PASC)(ACSC)(H2O)]Cl$_2$	Redish brown	435.49	54.38	11.93 (11.69)	22.04 (21.91)	4.59 (4.60)	19.28 (19.24)	18.37 (18.35)
[Cr (PASC) (BZSC)(H_2O)]Cl$_2$	Green	484.49	68	10.89 (10.73)	(29.73) 29.40	(3.71) 3.87	(17.33) 17.20	16.19 (16.25)
[Cr(PASC) (ACPHSC) (H_2O)]Cl$_2$	Red	498.49	55.45	10.42 (10.37)	31.29 (31.21)	3.81 (3.83)	16.85 (16.89)	15.64 (15.59)
[Cr(PASC) (CYSC)(H_2O)]Cl$_2$	Brown	476.49	67.34	10.91 (10.97)	27.70 (27.45)	4.19 (4.16)	17.62 (17.69)	16.29 (16.25)

Spectral Properties

1. Electronic Spectra

The electronic spectral data of mixed ligand complexes of chromium (III) is represented in table 3.

Complex of pyruvic acid semicarbazone and acetone semicarbazone

The first spin-allowed transitions (v_1) whose energy is assumed to be equal to 10Dq is observed at 11417 cm^{-1} in our Cr(III) complex. The second spin-allowed transition (v_2) has been assigned to the transition peak observed at 16722 cm^{-1}. Both v_1 and v_2 bands are some what but do not show any sign of splitting. The broadening of these bands may be due to a small distortion from octahedral structure.

Complex of pyruvic acid semicarbazone and benzaldehyde semicarbazone

The electronic spectrum of the Cr(III) complex exhibits band at 8718cm^{-1} which may be assigned to $^6A_1 \rightarrow {}^4T_1g$ (^4G), $^6A_1g \rightarrow {}^4E_2g$ (^4G) transitions and 14662 cm^{-1}, 30395cm^{-1} bands assigned for $^4A_2g \rightarrow {}^4T_2g$, $^4A_2g \rightarrow {}^4T_2g$ transitions, respectively. The position of these bands is consistent with a distorted octahedral geometry with D4h symmetry.

Complex of pyruvic acid semicarbazone and acetophenone semicarbazone

The Cr(III) complex exhibit three bands at 32154 cm$-^{1}$, 16722cm^{-1} and 9389cm^{-1} assigned to $^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(P)$, $^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(F)$, and $^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(P)$ transitions, respectively. The magnetic moment 3.618 B.M. was well within the range for the three unpaired electrons. The electronic spectral bands and the magnetic moment strongly support the octahedral geometry around the Cr(III) ion.

Complex of pyruvic acid semicarbazone and cyclohexanone semicarbazone

The electronic spectra of Cr(III) complexes exhibits bands in the range 16722, 23696 and 32154cm^{-1} with ν_2/ ν_1 ratio 1.417 corresponding to $^{6}A_{1}g \rightarrow {}^{4}T_{1}g$ (^{4}G), $^{6}A_{1}g \rightarrow {}^{4}E_{2}g$ (^{4}G), $^{4}A_{1}g$ (^{4}G) and $^{6}A_{1}g \rightarrow {}^{4}E_{2}g(^{4}D)$ transitions, respectively suggesting octahedral environment around Cr(III) ion.

IR spectra

Ligand/ Complex	**ν_{OH} (H2O)**	**ν_{NH2}**	**ν C= O (-COOH)**	**ν (NH)**	**ν C= O**	**ν C= N**	**ν N-H**	**ν N-N**	**ν C-O**	**ν M–N**	**ν M–O**
PYSC		3458	3145	2917	1713	1657	1570	1257	1140		
ACSC		3359		1785	1685	1580					
ACPHSC		3476		1749	1671	1558					
BZSC		3346	-	1745	1645	1580					
CYSC		3458		2917	1713	1671	1570	1291			
[Cr(PASC)(ACSC) (H2O)]Cl_2	3544	3344	3195	1761	1657	1546	1079	867	644	874	731
[Cr(PASC)(BZSC) (H_2O)]Cl_2	3592	3349	3193	1705	1644	1539	1134	873	721	879	734
[Cr(PASC)(ACPHSC) (H_2O)]Cl_2	3652	3455	3203	1731	1651	1557	1114	953	751	877	733
[Cr(PASC)(CYSC) (H_2O)]Cl_2	3720	3461	3168	2917	1708	1644	1534	1287	1125	879	734

Magnetic Properties

The 3d^{3} Cr(III) ion has three unpaired electrons and it’s complexes have magnetic moment close to the spin-only value of 4.173- 3.87 B.M. The temperature independent paramagnetism (TIP) contribution to the susceptibility of the ions is practically negligible in comparison with the curie law. As the ground term of Cr (III) is $^{4}A_{1g}$, the moment is temperature independent.

The magnetic moment 4.172-3.872B.M. observed for our Cr (III) complexs is slightly more than the spin-only value.

Magnetic susceptibility data of mixed ligand complexes

Name of Complex	**χ_g incm^3 mol^{-1}x 10^{-6}**	**Mol.wt of complex**	**χ_M in cm^{3}mol^{-1} x 10^{-6}**	**Pascal's correction (χ_L)x 10^{-6}**	**(χ_M-χ_L) x10^{-6}**	**μ_{eff}. In B.M.**
[Cr(PASC)(ACSC)(H2O)]Cl_2	17.159	400.91	6947.98	-204.39	7152.37	4.173
[Cr(PASC)(BZSC)(H_2O)]Cl_2	20.17	484.49	9773.71	-202.54	9979.25	4.879
[Cr(PASC)(ACPHSC)(H_2O)]Cl_2	10.56	498.49	5268.98	-220.61	5484.59	3.618
[Cr(PASC)(CYSC)(H_2O)]Cl_2	12.62	476.49	6024.68	-257.51	6282.19	3.872

Electrical conductivity

The maolar conductivity of the complexes are within the range 47-90Ω^{-1}cm^{2}mol^{-1} as shown in the table. Molar conductivity data shows electrolytic nature of the complexes.

Thermogravimetric Analysis

Thermo gravimetric analysis shows that Cr(III) shows loss of 3.841-4.210% within the temperature range 70 to 200^{o}C equivalent to 4,133% of loss for one water molecule. The weight loss in the respective range was owing to removal of the tightly bound water molecule in the vicinity of the complexes. This is supporting the octahedral geometry of the complexes. Positive value of entropy change shows increasing disordered nature of complexes.

Ligand/Complex	**Temp.^{0}C**	**% Mass Loss Found**	**DSC peak in^{0}CEndo/Exo**	**ΔH in J g^{-1}**	**$\Delta S^{\#}{}_{=\,-}\,\Delta H/T$ (Jg^{-1}K^{-1})**
[Cr(PASC)(ACSC) (H2O)]Cl_2	50-200 201-300 301-438.71	4.210 22.117 3.968	208.64	-444.21	1.5772
[Cr (PASC)(BZSC) (H_2O)]Cl_2	50-200 200-350 250-436.73	3.840 34.82 3.698	209.71	-444.21	1.160
[Cr(PASC)(ACPHSC) (H_2O)]Cl_2	100-250 250-400 400-800	4.128 16.673 5.478	343.34	-657.157	1.066
[Cr(PASC)(CYSC) (H_2O)]Cl_2	110-229 230-310	3.841 47.023	249.72	-5710.15	10.9238

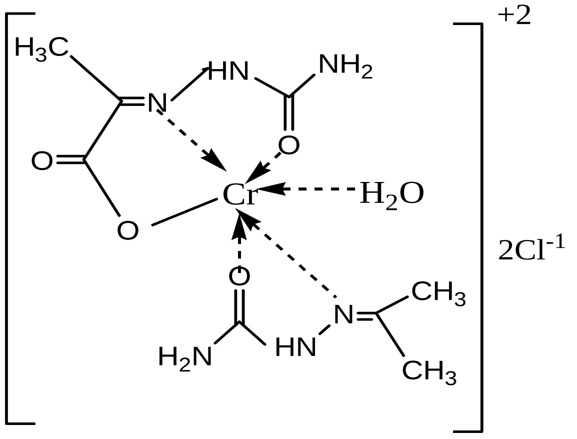
Microbiological Activities

The compound synthesized in the present investigation has been subjected to antimicrobial screening programs based on their structural features so as to ascertain their activity against five different microorganisms *E.coli., Baciullus Sp Staphylococcus sp., Pseudomonas Sp. and Proteus Sp.*

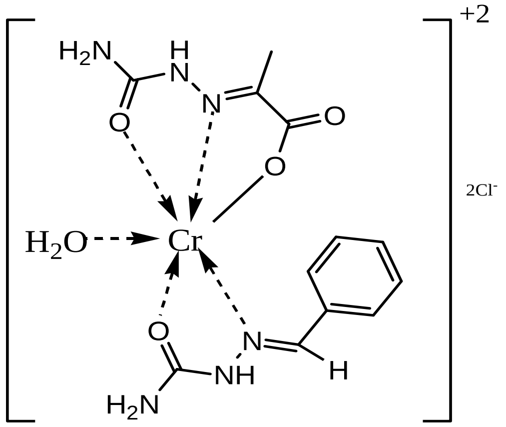
The solvent used was DMF and the sample concentrations were, 100ppm. The results of preliminary study on antimicrobial activity indicated that most of the compounds were highly and few were moderate active against these organisms.

Ligand/Complex	***E.coli.***	***Baciullus Sp.***	***Staphyloc-occus sp.***	***Pseudom-onas Sp.***	***Proteus Sp.***
(ACSC)	**6**	**4**	**6**	**8**	**5**
BZSC	7	10	9	13	8
(PASC)	**3**	**5**	**4**	**4**	**6**
[Cr(PASC)(ACSC)(H2O)]Cl$_2$	**7**	**7**	**8**	**6**	**8**
[Cr (PASC)(BZSC)(H_2O)]Cl$_2$	8	11	12	6	10
[Cr(PASC)(ACPHSC)(H_2O)]Cl$_2$	**8**	**11**	**12**	**6**	**10**
[Cr(PASC)(CYSC)(H_2O)]Cl$_2$	**7**	**10**	**10**	**09**	**07**

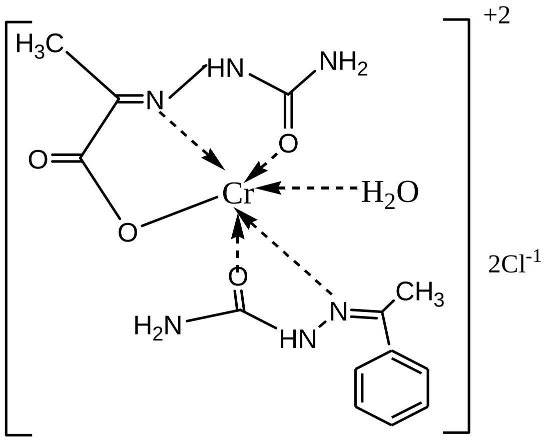
The proposed structure of complexes



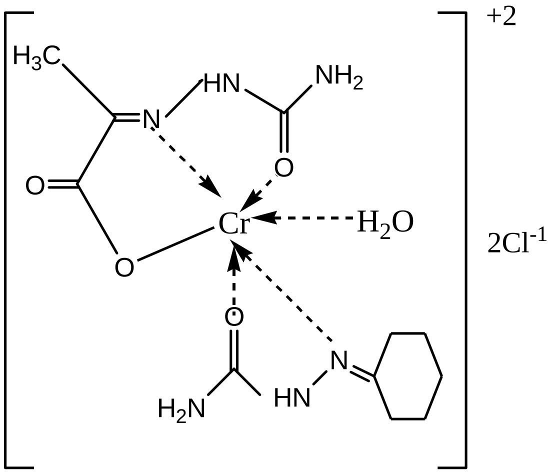
[Cr(PASC)(ACSC)(H_2O)]Cl$_2$



[Cr(PASC)(BZSC)(H_2O)]Cl$_2$



[Cr(PYSC)(ACPHSC)(H_2O)]Cl$_2$



[Cr(PASC)(CYSC)(H_2O)]Cl$_2$

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