



Thermochemical Study of Mixed Ligand Complexes Cyclohexanone Semicarbazone

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Abstract : The mixed ligand complexes of the type $[ML_1L_2]Cl_2$ have been synthesized, by the reactions of metal chlorides with two different ligands in 1:1:1 molar ratios. [Where $M=Cr(III),Co(II)$ and $Ni(II)$ $L_1=Pyruvic$ acid semicarbazone and $L_2=Cyclohexanonesemicarbazone$. 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.

Key words : Mixed ligand, cyclohexanone, pyruvic acid, semicarbazone, transition metals.

1.Introduction

Semicarbazone plays a key role in organic and biological chemistry. The semicarbazone linkage is an important functional group due to its extensive presence in natural products, pharmaceutical compounds and synthetic polymers.[1] The most common traditional method for the synthesis of the semicarbazone derivative is that semicarbazide hydrochloride on treatment with pyruvic acid or acetone gives semicarbazone derivative. Transition metal ions are playing an important role in biological processes in the human body[2]. For example, nickel(II), copper(II) and zinc(II) ions are the most abundant transition metals in humans. They are found either at the active sites or as structural components of a good number of enzymes[3]. The study of the coordination chemistry of biologically important metal ions with mixed ligands has been one of the recent developments in the field of bioinorganic chemistry. But, studies on the antimicrobial activities of their metal complexes are rare in literature.[4] Metal complexes containing nitrogen and sulphur donors have been proved to be potential antibacterial and fungal agents [5] as well as component of several vitamins and drugs[6,7].

It has been considerable interest in the studies of semicarbazone due to their coordination modes when bound to metals [8]. The wide applications and structural diversity of metal complexes of semicarbazone and thiosemicarbazone encouraged us to synthesize the tridentate ONO-donor semicarbazone ligands and their metal complexes. Metal complexes of pyruvic acid semicarbazone, semicarbazone of acetone, acetophenone, Benzaldehyde, cyclohexane, O-hydroxyacetophanone and their derivatives as ligands with transition metal as (ML_2) complexes have been already reported in early days.

Due to good chelating ability, the present work is mainly concerned on the studies of two novel semicarbazone, pyruvic acid semicarbazone $[L_1]$ and cyclohexanonesemicarbazone, $[L_2]$. The compositions of these semicarbazones were determined by the CHN and O analyses. For the characterization of these compounds we have used IR and UV spectral studies. We have synthesized 3d transition metal complexes of Cr (III), Mn (II), Fe(III), Co(II), Ni(II) and Cu(II) with pyruvic acid thiosemicarbazone $[L_1]$ and Benz aldehyde semicarbazone, $[L_2]$ in the ratio 1:1:1.

2. Synthesis

The compounds pyruvic acid semicarbazone and cyclohexanonesemicarbazone were prepared and characterized in the laboratory for the synthesis of mixed ligand complexes with transition metal chlorides. The metal chlorides of Cr(III), Mn (II),Co(II),Ni(II) and Cu(II) used were of analytical grade.

The following general procedure was used to prepare the mixed ligand complexes of pyruvic acid semicarbazone(PASC) and cyclohexanonesemicarbazone (CYSC) withCr(III),Fe(III),Mn(II),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 cyclohexanonesemicarbazone and 20 ml 0.01M pyruvic acid semicarbazone ligands were added with continuous stirring in a water bath. The 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. Add porcelain piece for heating the solution. Then the reaction mixture is refluxed with water condenser for two-three hours. Stirring was continued for another half an hour. The coloured precipitate of the complex separates out from the solution. The contents were cooled and the solid product of mixed ligand complex was filtered, washed thoroughly first with hot water and finally with ethanol and air dried, Yield is about 60-75%.

3. Analytical Properties

The resulting complexes were having different colors as given in the table 1, They are insoluble in chloroform, carbon tetrachloride, methanol, ethanol but soluble in DMF. The properties of complexes are also 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. From the magnetic moments these complexes show octahedral geometry.

Table .1: Characterization data of the complexes-

Ligand/ Complex	Colour	Mol. for.	Mole. wt	%Yield of the comp.	%of metal (Calculated)	%of C	%of H	%of N
Cr[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	Brown	CrC ₁₁ N ₆ O ₄ H ₂₀	476.49	67.34	10.91 (10.97)	27.70 (27.45)	4.19 (4.16)	17.62 (17.69)
Mn[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	Black	MnC ₁₁ N ₆ O ₄ H ₂₀	443.93	59.61	12.37 (12.32)	29.73(29.89)	4.50 (4.57)	18.92 (18.78)
Fe[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	Orange	FeC ₁₁ N ₆ O ₄ H ₂₀	480.35	71.21	11.62 (11.71)	27.47 (27.32)	4.16 (4.10)	17.48 (17.55)
Co[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	Brown	CoC ₁₁ N ₆ O ₄ H ₂₀	447.93	73.20	13.15 (13.29)	29.46 (29.61)	4.46 (4.51)	18.73 (18.82)
Ni[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	Green	NiC ₁₁ N ₆ O ₄ H ₂₀	447.69	69.25	13.22 (13.46)	29.55 (29.46)	4.46 (4.47)	18.76 (18.68)
Cu[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	Green	CuC ₁₁ N ₆ O ₄ H ₂₀	452.54	70.12	14.04 (14.04)	29.16 (29.28)	4.41 (4.47)	18.56 (18.47)

The conductances of the complexes are very low ($11.26-49.9\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at 29°C and $11.26-56.309\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at 39°C) indicating their non-electrolyte nature.

The amount of metals present in complexes were determined volumetrically by EDTA using double burette technique for optimum utilization of reagents. Indicator Erich Rome Black T was used for Mn (II), ammonium thiocyanate for Fe(III), xylenol orange for Co(II) and Cr(III), murexide for Ni(II) and Cu(II). Carbon, hydrogen and nitrogen analysis were carried from SAIF, Mumbai AND 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 L_1 and L_2 . 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.

4.4 Spectral Properties

4.4.1. Electronic Spectra

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

Table .2: Electronic Spectra

Sr.no.	Name of the Complex	v1	v2	v3	v2/ v1
1	Cr[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	16722	23696	32154	1.417
2	Mn[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	11655	21739	31746	1.865
3	Fe[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	8635	19607	26881	2.270
4	Co[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	8530	11603	14990	1.364
5	Ni[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	10810	17513	32362	1.620
6	Cu[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	8849	14224	32786	1.60

Table.2a Electronic transitions in (PASC)and (CYSC) complexes.

Sr. No	Name of the Complex	Absorbance wavelength in nm	Electronic transition	Geometry of the complex	Magnetic moment
1	Cr[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	16722	${}^6A_{1g} \rightarrow {}^4T_{1g} ({}^4G)$,	octahedral	3.872
		23696	${}^6A_{1g} \rightarrow {}^4E_{2g} ({}^4G), {}^4A_{1g} ({}^4G)$		
		32154	${}^6A_{1g} \rightarrow {}^4E_{2g} ({}^4D)$,		
2	Mn[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	11655	$6A_{1g} \rightarrow 4T_{1g}$	octahedral	4.931
		21739	$6A_{1g} \rightarrow 4T_{2g} (v_2)$		
		31746	$6A_{1g} \rightarrow 4A_{1g}$		
3	Fe[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	8635	${}^6A_{1g} \rightarrow {}^4T_{1g}$		5.632
		19607	${}^6A_{1g} \rightarrow {}^4T_{2g}$		
		26881	${}^6A_{1g} \rightarrow {}^4T_{1g} (P)$		
4	Co[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	8530	${}^4T_{1g} \rightarrow {}^4T_{2g} (F)$	octahedral	4.116
		11603	${}^4T_{1g} \rightarrow {}^4A_{2g} (F)$		
		14990	${}^4T_{1g} (F) \rightarrow {}^4T_{2g} (F)$.		
5	Ni[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	10810	${}^3A_{2g} \rightarrow {}^3T_{2g} (F)$	octahedral	3.891
		17513	${}^3A_{2g} (F) \rightarrow T_{1g} F$		
		32362	${}^3A_{2g} \rightarrow {}^3T_{1g} (P)$		
6	Cu[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	8849	${}^2B_{1g} \rightarrow {}^2A_{1g}$	octahedral	2.101
		14224	${}^2B_{1g} \rightarrow E_g$		
		3278	Charge transfer band		

Table 4.2b: Data and calculated transition energies (in cm^{-1}) of the spin allowed bands in mixed ligand complexes of pyruvic acid semicarbazone and cyclohexanonesemicarbazone.

Complex	Method of calculation	Obs. and cal. transition energies			B_{35}	β_{35}	LFSE in Kcal/mole	10Dq
		ν_1	ν_2	ν_3				
Cr[(PYSC) ₁ (CYSC) ₁ (H ₂ O) ₁]	Expt.	16722	23696	32154			20.06	16722
	(a)	10Dq	28492	34007	707	0.770	20.06	16722
	(b)	10Dq	22639	38332	378	0.412	20.06	16722
	(c)	10Dq	17798	38051	1646	1.793	20.06	16722
Co[(PYSC) ₁ (CYSC) ₁ (H ₂ O) ₁]	Expt	8530	11603	14990			6.71	11196
	(a)	8034	14249	15237	494	0.5096	4.82	8034
	(b)	8034	12496	19716	540	0.551	6.70	8034
	(c)	17995	26855	41760	985	1.015	10.79	17995
	(d)	9765	16041	27510	950	0.9787	5.85	9765
Ni[(PYSC) ₁ (CYSC) ₁ (H ₂ O) ₁]	Expt	10810	17513	32362			12.49	10416
	(a)	10Dq	18377	45990	1356	1.329	12.49	10416
	(b)	10Dq	17171	26688	611	0.5941	12.49	10416
	(c)	10Dq	19794	3115	941	0.8163	12.49	10416
	(d)	10Dq	14184	29676	1264	1.227	12.49	10416

Cr(III) Complex

The electronic spectra of Cr(III) complexes exhibits bands in the range 16722, 23696 and 32154 cm^{-1} with ν_2/ν_1 ratio 1.417 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. The value of 10Dq = 16722 cm^{-1} . Racha's parameter of interelectronic repulsion, $B_{35} = 910$. The nephelauxetic parameter $\beta_{35} = 0.9916$ which is less than unity indicating π -type of interactions between the metal and the ligand.

Mn(II) complex:

The electronic spectra of the Mn(II) complexes exhibit three weak absorption bands for the transitions $6A_{1g} \rightarrow 4T_{1g}$ (ν_1) (~11655 cm^{-1}), $6A_{1g} \rightarrow 4T_{2g}$ (ν_2) (~21739 cm^{-1}), and $6A_{1g} \rightarrow 4A_{1g}$, $4E_g$ (ν_3) (31746 cm^{-1}). These absorptions are consistent with an octahedral geometry around Mn(II) in all of the complexes. The magnetic moment of the Mn(II) mixed-ligand complex is 4.931 B. M., which is somewhat lower than the limits of the spin-free value for five unpaired electrons indicating that the complex is high-spin d^5 -system with an octahedral structure.

Fe(III) complex:

The spectrum of octahedral Fe(III) has not been adequately characterized. The ground term is ${}^6A_{1g}$ in high spin complexes. The absence of any other spin sextet terms implies that all crystal field transitions from ${}^6A_{1g}$ will be spin-forbidden, as well as Laporte-forbidden. The intensities of these transitions are very weak. Fe(III) forms large number of complexes, mostly octahedral ones, and the octahedron may be considered as its characteristic coordination shell.

The spectrum of our Fe(III) complex consists of three bands 8635 cm^{-1} , 19607 cm^{-1} and 26881 cm^{-1} . The sharp band at 26455 cm^{-1} can be assigned to M \rightarrow L charge transfer transition. The first band is assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transition. The next two bands have been assigned to the pair of transitions to 4E_g (G) and ${}^4E_{2g}$ (4D) which are degenerate in octahedral symmetry.

Co(II) Complex:

The reflectance spectrum of Co(II) complex is characteristic of Co(II) in octahedral environment, exhibiting three bands at 8530, 11603 and 14990 cm^{-1} assigned to the ${}^4T_1(F) \rightarrow {}^4T_2g(F)$, ${}^4T_1(F) \rightarrow {}^4A_2g(F)$, ${}^4T_1g(F) \rightarrow {}^4T_2g(F)$. The spectral parameters further support for the octahedral geometry is provided by the ratio ν_2/ν_1 which is 1.364 nearer to 2.0 as required for octahedral stereochemistry. The Co(II) complex under present

${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively. Distorted octahedral structure of complexes show bands at these positions.

4.2. Infrared spectra:

IR spectral data is shown in table 3. The infrared spectra of the complexes formed are found to be comparable with each other, but are definitely different from that of the ligand. The sharp and strong bands observed for the ligands in the range 900-1400 cm^{-1} are also found with the complexes also weak and broad bands are observed in this region. In order to study the binding mode of the Schiff base ligand (PYSC and CYSC) to the metal ion in complexes, the IR spectrum of the free ligands was compared with the spectra of the complexes.

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

Ligand/ Complex	ν_{OH} (H ₂ O)	ν_{NH_2}	$\nu_{\text{(NH)}}$	$\nu_{\text{C=O}}$ Carboxy lic group	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{N-H}}$	$\nu_{\text{N-N}}$	$\nu_{\text{C-N}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-S}}$
PYSC		3458	2917	2362	1713	1657	1570	1257	1157			
CYSC		3458	2917	2358	1713	1671	1570	1291	1157			
Cr[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	3720	3461	2917	2354	1708	1644	1534	1287	1125	879	734	467
Mn[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	3691	3463	2917	2350	1710	1634	1539	1278	1134	869	735	464
Fe[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	3657	3458	2917	2356	1709	1654	1535	1289	1138	867	757	479
Co[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	3579	3456	2917	2349	1698	1623	1555	1287	1134	877	786	478
Ni[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	3598	3459	2917	2337	1697	1642	1537	1259	1142	883	763	470
Cu[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	3569	3462	2917	2343	1709	1629	1549	1261	1149	870	771	469

The spectrum of the ligand exhibits a medium band in the range 3458 cm^{-1} which is assigned to $\nu_{\text{(NH)}}$ vibration. The medium band at 2917 cm^{-1} in the free ligand due to $\nu_{\text{(NH)}}$ vibration indicates that the ligand remains in the keto form in the solid state. The presence of this band in the complexes indicates that there is no enolisation and deprotonation of the ligand and the semicarbazone is coordinated in the neutral form. A band at 1713 cm^{-1} in the ligand is shifted to lower frequency of about (4-16 cm^{-1}) in the complexes showing the involvement of C=O oxygen in coordination. The presence of bands in the 1657-1671 cm^{-1} region for complexes supports the keto form of ligand in all the complexes can be attributed to the characteristic >C=N-group. This band shift slightly towards lower frequencies from 1523-1556 cm^{-1} in the complexes, indicating the coordination of azomethine nitrogen to metal. It is further supported by the appearance of new bands at 867-873 cm^{-1} assignable to $\nu_{\text{(M-N)}}$ for the complex. The $\nu_{\text{(N-N)}}$ band of semicarbazone is observed to 1257 cm^{-1} . The increase in the $\nu_{\text{(N-N)}}$ value in the spectra of the complexes is due to the increase in double bond character, offsetting the loss of electron density via donation to the metal and it is a confirmation of the coordination of the ligand through the azomethine. In all complexes the asymmetric and symmetric stretching bands, corresponding to unidentate type of acetate group are present. For pyruvic acid semicarbazone bands observed at 3458 cm^{-1} , 2917 cm^{-1} , 2362, 1645 cm^{-1} , 1285 cm^{-1} , 1124 cm^{-1} and 1040 cm^{-1} are assigned for (NH₂), (-OH of carboxylic group), (C=O), (C=N), (N-N), (C-N) groups, respectively. While cyclohexanone semicarbazone indicating bands at 3458 cm^{-1} , 1713 cm^{-1} , 1657 cm^{-1} , 1570 cm^{-1} and 1259 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 2-21 cm^{-1} , (C=O) by 05-16 cm^{-1} , (C=N) by 13-32 cm^{-1} , (C-N) by 30-70 cm^{-1} . Other groups also shows some what lowering the frequencies due to change in the environment. Four new bands are observed, one for -OH group of H₂O within the range 3501-3612 cm^{-1} and three bands within the range of 857-871 cm^{-1} , 734-771 cm^{-1} and 464-469 cm^{-1} assigned for (M-O) and (M-N) bond formation. A broad band appears in the region at 3598-3720 cm^{-1} in all complexes indicating presence of the coordinated water molecule.

5. Magnetic Properties

The magnetic moments, μ_{eff} of the complexes are given in table 4 and 4a.

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

Ligand/ Complex	Magnetic moment	Molar cond. $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at room temp.(29 ⁰ C)	Molar cond. $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at room temp + 10 ⁰ C(39 ⁰ C)
Cr[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	3.872	29.4	33.7
Mn[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	4.931	22.2	22.5
Fe[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	5.632	11.11	11.26
Co[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	4.116	49.6	56.3
Ni[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	3.891	28.21	33.7
Cu[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	2.101	30.5	33.9

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

Complex	X_g incg s units $\times 10^{-6}$	Mol. wt of complex	X_M in cgsunitsx 10^{-6}	Pascal's correction 10^{-6}	$X_M \times 10^{-6}$	μ_{eff} In B.M.
Cr[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	12.62	476.49	6024.68	-257.51	6282.19	3.872
Mn[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	23.61	443.93	10483.25	-244.51	10727.11	4.931
Fe[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	27.02	480.35	12982.26	-257.51	13290.26	5.632
Co[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	15.30	447.93	6851.88	-244.51	7096.39	4.116
Ni[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	13.62	447.69	6099.03	-244.51	6343.54	3.891
Cu[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	3.54	452.54	1603.21	-244.51	1847.72	2.101

Cr(III) complex:

The 3d³ Cr(III) ion has three unpaired electrons and it's the complex have magnetic moment close to the spin-only value of 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 ⁴A_{1g}, the moment is temperature independent. The magnetic moment 3.872B.M. observed for our Cr (III) complexes is slightly more than the spin-only value.

Mn(II) complex:

3d⁵Mn (II) ion has the ⁶A_{1g} ground term, for which there is no reduction of the moment below the spin-only value of 5.92 B.M.. It is also independent of the stereochemistry around it. The observed magnetic moment 4.931B.M. of Mn(II) complex is less than that generally observed for spin-free d⁵ system. Such lower magnetic moments of Mn(II) complexes have been explained with the assumption of anti ferromagnetic interaction between manganese ion in the solids. The lower magnetic moment in the present Mn (II) complexes may be either due to the presence of antiferromagnetic exchange interaction between the manganese ions in the solid state or due to aerial oxidation of Mn(II) → Mn(III) during the preparation of the complex. In the absence of magnetic susceptibility data over a temperature range, nothing definitely can be said about the presence of anti ferromagnetic interaction.

Fe(III) complex:

In high-spin complexes, the magnetic moments are always very close to the spin-only value of 5.92 and are independent of temperature.

The observed magnetic moment 5.632 B.M. of Fe(III) complex is lower than the expected value. So Fe (III) must be high-spin in the complexes. The low magnetic moment might be due to the metal-metal interaction.

Co(II) Complex :

The magnetic moment of the mixed-ligand complex of Co(II) is 4.116B.M., which is higher than the expected value 3.87 B. M.. This increase may be due to the incomplete quenching of the orbital magnetic moment by the surrounding ligands and suggests an octahedral geometry around the Co(II) ion.

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 3.891B.M. suggesting octahedral structure for this complex. Magnetic measurements therefore support the deductions made from spectral studies.

Cu(II) complex:

The magnetic moment of the Cu(II) complex is observed at 2.101 B. M., which corresponds to a single unpaired electron with a very slight orbital contribution and suggests an octahedral geometry around the Cu(II) ion.

6.Electrical conductivity:

The conductances of the complexes are very low ($11.11-56.862\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) indicating their non-electrolyte nature.

7.Thermogravimetric Analysis

The thermo grams (TG) of the compounds have been recorded in flowing nitrogen atmosphere at the heating rate of $10^\circ\text{C}/\text{min}$ 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.

Table 4.5: Thermodynamic properties of complexes

Ligand/Complex	Temp. $^\circ\text{C}$	% Mass Loss Found	DSC peak in $^\circ\text{C}$ Endo/Exo	ΔH in J g^{-1}	$\Delta\text{S}^\#$
Cr[(PASC) $_1$ (CYSC) $_1$ (H $_2$ O) $_1$]	110-229 230-310	3.841 47.023	249.72	-5710.15	10.9238
Mn[(PASC) $_1$ (CYSC) $_1$ (H $_2$ O) $_1$]	120-240 241-320	3.941 44.631	249.05	-3095.27	5.9290
Fe[(PASC) $_1$ (CYSC) $_1$ (H $_2$ O) $_1$]	150-224 225-315	3.469 47.34	243.39	-8355.27	16.1636
Co[(PASC) $_1$ (CYSC) $_1$ (H $_2$ O) $_1$]	80-130 131-600	3.567 28.712	128.11	-616.83	1.5364
Ni[(PASC) $_1$ (CYSC) $_1$ (H $_2$ O) $_1$]	135-232 233-384	4.124 30.231	249.02	-1353.93	2.5936
Cu[(PASC) $_1$ (CYSC) $_1$ (H $_2$ O) $_1$]	85-195 200-285	4.0372 39.321	281.12	-2849.77	5.1428

Thermogravimetric analysis of complex chromium shows percentage loss of 3.841 in the temperature range $120-200^\circ\text{C}$ due to coordinated water molecule (3.781%), then within temp. range of $200-300^\circ\text{C}$ there is loss of 47% due to decomposition of the complex Mn(II) complex shows loss in weight of 3.941 in the range of temp. $120-240^\circ\text{C}$, while there is loss 44.63 % indicating decomposition of complex. Iron complex shows loss of 3.921 within the temperature range of $150-224^\circ\text{C}$ due to coordinated water molecule, after that upto 600°C there is net loss of 17.054. Co(II) shows loss in weight of 4.167 for theoretical loss of water of 4.017 within the range of $30-250^\circ\text{C}$. While Ni(II) indicates loss of 4.524 within the range of $135-224^\circ\text{C}$. and Cu(II) complex indicates loss of water molecule. with wt loss of 3.960 during temperature range $85-190^\circ\text{C}$. Co(II), Ni(II) and Cu(II) shows weight loss of 28, 30 and 39 % only within the temp. range $250-600^\circ\text{C}$. This is attributed for loss

of one water molecule in the complexes. which indicates the octahedral nature of complexes. Thermodynamic properties are shown in table 5.

8. Biological Activities.

The main objective of the synthesis of any antimicrobial compound is to inhibit the microbe without harming other biological cells. 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 deactivate enzymes responsible for respiration processes.

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, 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. Ni(II) and Cu(II) complexes are considerably active than ligands as compared to other complexes.

Microbial activities are shown in table 6

Table 6 Biological Activities of Ligands

Ligand/Complex	E.coli.	Baciullus Sp.	Staphylococcus sp.	Pseudomonas Sp.	Proteus Sp.
Pyruvic acid semicarbazone	3	5	4	4	6
Cyclohexanone Semicarbazone	6	8	7	12	9
Cr[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	7	10	10	09	07
Mn[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	8	9	11	10	10
Fe[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	10	10	11	09	12
Co[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	9	11	14	10	12
Ni[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	11	10	14	16	16
Cu[(PASC) ₁ (CYSC) ₁ (H ₂ O) ₁]	17	13	13	18	17

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