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Studies of the Structural and Biological Profile of some transition metal ion complexes

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Abstract

Semicarbazones and thiosemicarbazones are potent intermediates for the synthesis of bioactive materials. They are used extensively in medicinal chemistry. The present paper attempts to report the synthesis, characterization and biological activities of complexes of Co(II), Ni(II) and Cu(II) with 2-furfural 4-methylsemicarbazone (HFMS). The ligands and complexes have been synthesized in the laboratory. The complexes formed are characterized by microanalysis, conductivity measurement, magnetic dipole moment, FTIR spectra and electronic spectra. In all the complexes, ligand semicarbazone acts as monoanionic bidentate which coordinates through azomethine nitrogen(C=N) and deprotonated oxygen and forms a 5-membered ring with the metal ions. The geometry of complexes has been found to be distorted octahedral. The biological activities of semicarbazones and thiosemicarbazones increase on coordination with transition metal ions due to the chelating effect. The biological activity of ligand complexes has been found against the standard (chloramphenicol).

Keywords: *HFMS, metal complexes, distorted octahedral, antibacterial.*

I. Introduction

Metal complexes play a very important role in drug development and medicinal chemistry[1-2]. We have seen that coordination compounds have been used as a potential drug because transition metals play a very important role in the normal functioning of living organisms[3]. The growth of coordination chemistry with the development of supporting ligands affects the reactivity and stability of the metal complexes in the primary coordination sphere[4]. The features of the structures and bonding of the different Schiff base complexes give a better understanding of the complex life processes. In coordination chemistry, the Schiff bases are extensively appplied as ligands because they contain various donor atoms like N, O and S depicting broad pharmaceutical activities[5-6]. The Schiff bases of semicarbazide and thiosemicarbazide with the transition metals show a wide range of coordination modes which are affected by the number and the type of substituents[7-8]. We all know that semicarbazide compounds containing the amide moiety are highly capable of forming metal complexes[9].

Semicarbazones Schiff bases, present as keto and enol tautomeric forms, are in equilibrium. They act as a neutral ligand by the nitrogen atom of the imine group or the oxygen atom of the carbonyl group or as a monoanionic ligand[10-12]. The structural possibilities of the semicarbazone Schiff base may be increased with different substituent groups. This includes new sites of bonding, increasing the possibility of coordination with metal ions[13-14]. The versatile structural possibilities of semicarbazone, thiosemicarbazone and their derivatives have been responsible for their applications of these compounds in antimicrobial, antiseptic, antiviral, anticonvulsant, antitumour and anti-inflammatory efficacy[15-18]. Semicarbazones and thiosemicarbazones are N, O and S containing organic ligands which are of tremendous interest in the discipline of chemistry and biology. Because of the chelating nature and pharmaceutical properties of semicarbazone complexes, they have been studied broadly in recent years.

The significance of semicarbazone complexes has enabled us to set about the study that involves the synthesis, characterization and biological activities of the complexes of Co(II), Ni(II) and Cu(II) with 2-furfural 4-methylsemicarbazone (HFMS).

II. Experimental

All the chemicals we used, were of A.R. grade quality.

Synthesis of Ligand (2-furfural 4-methylsemicarbazone)

10 ml of furfural and 15 ml of 4-methylsemicarbazone were taken in the R.B. flask. The pH of the solution was maintained at 3.0 by using acetic buffer. The solution was refluxed for an hour then light-yellow ppt. was

obtained. The ppt. formed was filtered and cleaned with ethanol then dried over anhydrous $CaCl_2$ in a desiccator. The crude sample was recrystallized in ethanol.

Synthesis of metal complexes

0.2 mole of ligand 2-furfural 4-methylsemicarbazone (HFMS) was dissolved in 15 ml of ethanol. 0.1 mole of metal chlorides of Co(II), Ni(II) and Cu(II) dissolved in 15ml of ethanol separately. These two solutions are taken in the R.B. flask. In this solution about 0.2ml of α-picoline was added followed by the addition of 10ml of sodium acetate, making medium alkaline. The mixed solution was refluxed for 3-4 hours. Then it was cooled and stirred for an hour with a magnetic stirrer. The precipitate that appeared was filtered and cleaned with ethanol then dried over anhydrous $CaCl_2$ in a desiccator. The yield was 80-90%.

Analysis and measurements

The contents of Carbon, Hydrogen and Nitrogen in each sample were analyzed micro-analytically at IIT, Patna. The molar conductivity was measured at R.T. in DMF solution using a Torshniwal conductivity bridge with a dip-type cell with a smooth Pt-electrode of the cell content 1.02. The magnetic dipole moments were measured using Gouy's method, Mercury(II)tetracyanocobaltate as calibrant at IIT, Patna. The FTIR spectra were recorded in KBr on a Perkin-Elmer 577 spectrophotometer. The electronic spectra of complexes were recorded in DMF in Beckman DU-6 spectrophotometer at IIT, Patna. The analytical data of the ligand and complexes have been placed in Table 1.

III. Result and Discussion

The micro-analytical data reveals that the general formula of the complexes formed is $[ML_2(\alpha\text{-pico})_2]$. Where,
M = Co(II), Ni(II) and Cu(II)
and L = HFMS (2-furfural 4-methylsemicarbazone).
All the complexes are coloured and insoluble in water but soluble in DMF, alcohol and chloroform. The molar conductance values of the complexes suggest that all these complexes have a non-electrolytic character. The magnetic studies of complexes at R.T. are in agreement with octahedral geometry for Co(II), Ni(II) and Cu(II). All the complexes exhibit a paramagnetic nature.

Analytical Table- 1

S.No.	Complexes	% of M	% of C	% of H	% of N	% of O	Colour	Molar Conductance $(\Omega^{-1}cm^{-2}mol^{-1})$	μeff (B.M.)
1.	Ligand ($C_7H_9N_3O_2$)		50.210 (50.299)	5.307 (5.389)	25.098 (25.149)	19.385 (19.161)			
2.	$Co(C_7H_8N_3O_2)_2(C_6H_7N)_2$	10.203 (10.225)	54.012 (54.072)	5.152 (5.199)	19.400 (19.410)	11.233 (11.091)	Faint brown	18	4.56
3.	$Ni(C_7H_8N_3O_2)_2(C_6H_7N)_2$	10.121 (10.178)	54.082 (54.100)	5.186 (5.202)	19.382 (19.420)	11.229 (11.097)	Pale green	18	3.20
4.	$Cu((C_7H_8N_3O_2)_2(C_6H_7N)_2$	10.896 (10.920)	53.608 (53.654)	5.126 (5.159)	19.206 (19.260)	11.164 (11.006)	Deep green	18	1.96

FTIR Spectra

The coordination modes of ligands were obtained by the comparison of IR spectra of the metal complexes with that of free ligands. The important absorption bands with their most probable assignments to the different groups are shown in Table 2.

The sharp and strong band at 3450 cm^{-1} of the free ligand is assigned to ν_{OH}[19]. The sharp band at 3325 cm^{-1} and 3400 cm^{-1} were assigned to ν_{N-H} (sym) and ν_{N-H} (asym) respectively[20]. The band at 1700 cm^{-1} was assigned to $\nu_{C=O}$[21]. The band at 1650 cm^{-1} (medium) may be assigned to $\nu_{C=N}$ (azomethine)[22]. A strong band at 1300 cm^{-1} was probably due to ν_{C-O} vibration[23]. The band at 3450 cm^{-1} (ν_{OH}), 3200 cm^{-1} (ν_{N-NH}), 1700 cm^{-1} ($\nu_{C=O}$) and 1300 cm^{-1} (ν_{C-O}) in the spectra of the ligand (HFMS) reveals that the ligand exists in two tautomeric forms: keto form and enol form. The enol form should be more stable due to increased conjugation.

In all the complexes ν_{N-H} (sym) and ν_{N-H} (asym) absorption bands do not show appreciable change, indicating the non-coordination of N of $-NHCH_3$ group of the ligand (HFMS)[20,24]. The decrease in the frequency of $\nu_{C=N}$ (azomethine) by 15-20 cm^{-1} in all the complexes indicates that the ligand coordinates through azomethine moiety in the complexes[25]. The disappearance of bands due to ν_{OH}, $\nu_{N\text{-}NH}$ and $\nu_{C=O}$ and the increase in the absorption frequency of $\nu_{C\text{-}O}$ by 50-58 cm^{-1} show that ligand coordinates through deprotonated –OH group in the complexes. The appearance of new bands in the complexes 1525-1535 cm^{-1} and 300-315 cm^{-1} are the characteristic bands for coordinated picoline[26].

Thus, all the complexes are six coordinated complexes. The ligand behaves as monoanionic bidentate coordinated through azomethine nitrogen and deprotonated oxygen.

Analytical Table- 2

I.R. bands with their assignment of free ligand 2-furfural 4-methylsemicarbazone (HFMS).

S.No.	Complexes	ν_{OH}	$\nu_{N\text{-}NH}$	$\nu_{C=N}$	$\nu_{C=O}$	$\nu_{C\text{-}O}$	Others	$\nu_{N\text{-}H}$ (sym)	$\nu_{N\text{-}H}$ (asym)
1.	Ligand	3450 cm^{-1}	3200 cm^{-1}	1650 cm^{-1}	1700 cm^{-1}	1300 cm^{-1}		3325 cm^{-1}	3400 cm^{-1}
2.	$Co(HFMS)_2(\alpha\text{-}pico)_2$	Disappeared	Disappeared	1630 cm^{-1}	Disappeared	1350 cm^{-1}	1530 cm^{-1} 300 cm^{-1}		
3.	$Ni(HFMS)_2(\alpha\text{-}pico)_2$	Disappeared	Disappeared	1630 cm^{-1}	Disappeared	1358 cm^{-1}	1535 cm^{-1} 310 cm^{-1}		
4.	$Cu(HFMS)_2(\alpha\text{-}pico)_2$	Disappeared	Disappeared	1635 cm^{-1}	Disappeared	1350 cm^{-1}	1525 cm^{-1} 315 cm^{-1}		

Magnetic dipole moment and Electronic Spectra

The value of the magnetic dipole moment of the Co(II) complex have been found to be 4.56 B.M., which suggest paramagnetic nature and octahedral geometry for Co(II) complex[27]. This value also suggests that complex is high spin complex. The ground term for Co(II) high spin complex is ^4F, which show the following three possible transitions in the electronic spectra of the complex. These bands are assigned as below.

$^4T_{1g} \rightarrow {}^4T_{2g}$, $\upsilon_1 = 8680\ cm^{-1}$,
$^4T_{1g} \rightarrow {}^4A_{2g}$, $\upsilon_2 = 17000\ cm^{-1}$,
and $^4T_{1g} \rightarrow {}^4T_{1g}\ (P)$, $\upsilon_3 = 21000\ cm^{-1}$.

The nephelauxetic effect, $\beta = \frac{B\ in\ complex}{B\ in\ free\ metal\ ion} = \frac{952.3}{1120} = 0.85$.

This value indicates a little covalency in the metal-ligand bond and confirms the distorted octahedral geometry of the complex.

The magnetic dipole moment value of the Ni(II) complex is found to be 3.20 B.M., which is more than the expected value due to the first-order Zeeman effect[28]. The ground term of Ni(II) is ^3F, which splits in weak octahedral field $^3A_{2g}$ as a ground term. The electronic spectra of several reported[29,30] distorted octahedral complexes suggest that the complex has distorted octahedral geometry. The following three transitions have been found for the Ni(II) complex, which is shown below.

$^3A_{2g} \rightarrow {}^3T_{2g}$, $\upsilon_1 = 9210\ cm^{-1}$,
$^3A^{2g} \rightarrow {}^3T_{1g}\ (F)$, $\upsilon_2 = 16100\ cm^{-1}$,
and $^3A^{2g} \rightarrow {}^3T_{1g}\ (P)$, $\upsilon_3 = 24690\ cm^{-1}$.

The ratio of $\upsilon_2/\upsilon_1 = \frac{16100}{9210} = 1.748$, which is required for octahedral geometry.

The Nephelauxetic effect, β = 0.84, represents a slightly covalent character. These values are in a close agreement with the required value for a distorted octahedral complex.

The magnetic dipole moment value of the Cu(II) complex is 1.96 B.M., which represents that the Cu(II) complex is paramagnetic with one unpaired electron and has octahedral geometry. The electronic spectra of Cu(II) complexes have been explained by the crystal field model[31,32]. The ground term for Cu(II) is ^2D, which splits in crystal field as ^2E_g and $^2T_{2g}$. The two bands in the spectra in the given complex have been found at 15800 cm^{-1} and 26250 cm^{-1}, which represents the one transition as $^2T_{2g} \rightarrow {}^2E_g$, $\upsilon = 15800\ cm^{-1}$ and the other is at 26250 cm^{-1} was recognized as charged transfer band. These values are in close agreement with the distorted octahedral geometry of the Cu(II) complex.

Biological Profile of ligand and their complexes

The ligand and their complexes were tested for vitro antibacterial activities against Escherichia coli and Citrobacter gillenii applying the agar disk diffusion method[33]. As a standard the chloramphenicol, an antibiotic has been taken up for comparing the effect of ligand and their complexes. Firstly, the test compound was dipped in DMSO solution, then a PSTrail petri dish was poured with Autoclave Nutrient agar medium. At 35°C the dish was incubated for 24 hours, then the growth in the zone of inhibition around the dish was measured. Here DMSO was used as a solvent so it was also tested against the whole organism but no activity was found. The data of antibacterial activity has been shown in Table 3.

It is evident from the data (given in table 3) that all complexes exhibit much increased biological activity compared to the ligand, but lower than the standard at all the concentrations. The complexes of Cu(II) are found to be more active than other complexes at all concentrations. This may be a result of enhanced biological activity of Cu(II) than Co(II) and Ni(II). The enhanced biological activity of complexes than ligands may be due to chelate formation which captivates the complex across the cell membrane[34,35].

Analytical Table- 3

Antibacterial activity data of ligand and complexes inhibition zone ion (ml)

S.N.	Compound	E-coli concentration			Citrobacter gillenii concentration		
		500 µg/ml	250 µg/ml	100 µg/ml	500 µg/ml	250 µg/ml	100 µg/ml
1.	Standard (Chloramphenicol)	40	39	33	35	34	30
2.	Ligand (HFMS)	8	7	5	9	8	6
3.	$Co(HFMS)_2(\alpha\text{-pico})_2$	11	10	7	12	10	9
4.	$Ni(HFMS)_2(\alpha\text{-pico})_2$	13	12	9	14	12	11
5.	$Cu(HFMS)_2(\alpha\text{-pico})_2$	17	16	13	17	15	13

IV. Conclusions

The ligand ($C_7H_9N_3O_2$) behaves like mono-anionic bidentate and coordinates with the metal ion through azomethine nitrogen and deprotonated oxygen to form a 5-membered ring. As the different axial ligands were present in all, the complexes are considerably tetragonally distorted. The measurement of biological profile discloses that all the complexes of Co(II), Ni(II) and Cu(II) are more biologically active compared to the free ligand but less active than the standard (chloramphenicol).

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