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Spectroscopic Investigation and Antifungal Studies of Some Mixed Ligand Complexes of Co(II), Ni(II) and Cu(II) with 6-Methyl-2-pyridyl Formamide Semicarbazone and Thiosemicarbazone

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Complexes of Co(II), Ni(II) and Cu(II) with 6-methyl-2-pyridyl formamide semicarbazone and 6-methyl-2-pyridyl formamide thiosemicarbazone formed by the condensation of semicarbazide hydrochloride/thiosemicarbazide hydrochloride with 6-methyl-2-pyridyl formamide have been synthesized and their physicochemical properties have been investigated by elemental analysis, magnetic measurements, molar conductance, electronic spectra and infrared spectra. It has been observed that the ligands coordinated to the metal ion in a tridentate fashion through the nitrogen and oxygen/sulphur atoms. The ligands, 6-methyl-2-pyridyl formamide semicarbazone, 6-methyl-2-pyridyl formamide thiosemicarbazone as well as metal complexes have been screened for antifungal activity on *Aspergillus flavus* and *Aspergillus niger*.

Key Words: Co(II), Ni(II) and Cu(II) complexes, 6-Methyl-2-pyridyl formamide semicarbazone, 6-Methyl-2-pyridyl formamide thiosemicarbazone, Antifungal study.

INTRODUCTION

Semicarbazone and thiosemicarbazone and their metal complexes have been extensively used in many biological processes[1–4] such as anti-tubercular[5, 6], anti-inflammatory[7], anti-cancerous[8] and pharmacological[9, 10] and many important vital enzymatic metals present in the cell[11]. In continuation of previous work[12–17] on transition metal complexes with semicarbazone and thiosemicarbazone ligands, the present paper describes the synthesis of Co(II), Ni(II) and Cu(II) complexes with ligand 6-methyl-2-pyridyl formamide semicarbazone (MPFS) and 6-methyl-2-pyridyl formamide thiosemicarbazone (MPFTS). The ligands of MPFS/MPFTS as well as their metal complexes are tested for their antifungal activity.

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EXPERIMENTAL

All the chemicals used were of AnalaR grade. The ligands as well as metal complexes were analyzed according to standard methods[18]. The infrared spectra were recorded on Beckmann IR-20 spectrophotometer using KBr pellets. Electronic spectra were recorded on Cary-2390 spectrophotometer, conductivity measurement were carried out on Toshniwal conductivity bridge using 10^{-3} M DMF solution, magnetic susceptibility was measured at 300 ± 1 K on a Gouy balance using mercury tetraisothiocyanato cobaltate as a calibrant. The analytical data, colour, magnetic susceptibility, electronic spectra and conductivity data are recorded in Table-1.

TABLE-1
ANALYTICAL, COLOUR, MAGNETIC MOMENT, ELECTRONIC SPECTRA AND CONDUCTIVITY MEASUREMENT DATA FOR METAL COMPLEXES OF THE TYPE $[M(MPFS)_2]X_2$ and $[M(MPFTS)_2]X_2$

Compound (Colour)	% Analysis Found (Calcd.)				μ_{eff} (B.M.)	Ω_m (ohm^{-1} cm^2 mol^{-1})	λ_{max} (electronic) (cm^{-1})
	M	C	N	H			
MPFS (Yellow)	–	50.12 (50.00)	36.34 (36.45)	5.25 (5.20)	–	–	–
MPFTS (Colourless)	–	46.28 (46.15)	33.77 (33.65)	4.74 (4.80)	–	–	–
$[Co(MPFS)_2]Cl_2$ (Red)	11.43 (11.46)	37.46 (37.35)	27.32 (27.24)	3.92 (3.89)	5.09	104	8600, 12400, 20000
$[Co(MPFTS)_2]Cl_2$ (Orange)	10.73 (10.79)	35.31 (35.16)	25.73 (25.64)	3.69 (3.66)	5.18	107	8500, 12700, 20300
$[Co(MPFS)_2]Br_2$ (Brown)	9.85 (9.77)	31.97 (31.85)	23.33 (23.22)	3.35 (3.31)	5.12	95	8700, 12500, 20100
$[Co(MPFTS)_2]Br_2$ (Green)	9.22 (9.28)	30.11 (30.15)	21.94 (22.05)	3.62 (3.66)	5.10	99	8400, 12800, 20400
$[Co(MPFS)_2]I_2$ (Reddish brown)	8.52 (8.45)	27.68 (27.55)	20.18 (20.09)	2.84 (2.87)	4.72	101	8800, 12300, 20500
$[Co(MPFTS)_2]I_2$ (Brown)	8.01 (8.08)	26.47 (26.34)	19.32 (19.21)	2.77 (2.74)	4.77	106	8300, 12600, 20600
$[Ni(MPFS)_2]Cl_2$ (Yellowish red)	11.44 (11.42)	37.49 (37.37)	27.34 (27.25)	3.86 (3.89)	3.24	110	11300, 16400, 22600
$[Ni(MPFTS)_2]Cl_2$ (Yellowish brown)	10.82 (10.75)	35.30 (35.18)	25.49 (25.65)	3.63 (3.66)	3.27	113	11500, 16700, 22800
$[Ni(MPFS)_2]Br_2$ (Reddish brown)	9.83 (9.74)	31.79 (31.86)	23.31 (23.23)	3.35 (3.31)	3.33	116	11400, 16900, 23000
$[Ni(MPFTS)_2]Br_2$ (Reddish brown)	9.17 (9.25)	30.13 (30.25)	21.92 (22.06)	3.18 (3.15)	3.36	118	11700, 17200, 23300

Compound (Colour)	% Analysis Found (Calcd.)				μ_{eff} (B.M.)	Ω_m (ohm^{-1} cm^2 mol^{-1})	λ_{max} (electronic) (cm^{-1})
	M	C	N	H			
$[Ni(MPFS)_2]I_2$ (Brown)	8.49 (8.42)	27.67 (27.56)	20.18 (20.09)	2.82 (2.87)	3.21	119	11600, 17000, 23200
$[Ni(MPFTS)_2]I_2$ (Deep brown)	9.32 (9.25)	30.13 (30.25)	22.17 (22.06)	3.11 (3.15)	3.26	121	11200, 17100, 23100
$[Cu(MPFS)_2]Cl_2$ (Green)	12.33 (12.25)	37.16 (37.03)	27.11 (26.99)	3.89 (3.85)	1.89	126	15700, 26700
$[Cu(MPFTS)_2]Cl_2$ (Dark green)	11.48 (11.54)	34.73 (34.87)	25.34 (25.42)	3.66 (3.63)	1.86	127	15400, 26900
$[Cu(MPFS)_2]Br_2$ (Greenish brown)	10.38 (10.46)	31.76 (31.61)	23.14 (23.05)	3.34 (3.29)	1.93	120	15100, 27000
$[Cu(MPFTS)_2]Br_2$ (Greenish red)	11.17 (11.11)	33.48 (33.50)	24.58 (24.49)	3.53 (3.49)	1.97	124	15900, 27300

Preparation of the ligands, MPFS and MPFTS: Ethanolic solutions of 6-methyl 2-pyridyl formamide was added to semicarbazide hydrochloride/thiosemicarbazide hydrochloride dissolved in 10% ethanolic solution of sodium acetate. The reaction mixtures were stirred and refluxed for 4–5 h, when bright yellow crystals separated in the case of semicarbazone and colourless crystals in case of thiosemicarbazone. The crystals were washed with ethanol and dried in an electric oven at *ca.* 60°C. (Yield 70–75%).

Preparation of the metal complexes: An ethanolic solution of the corresponding metal halides, refluxed with ethanolic solutions of the ligands MPFS/MPFTS in the molar ratios 1 : 2 for 2–3 h. The complexes were cooled, filtered and washed with ethanol several times to remove any excess of the metal halides or ligand. Finally the complexes were washed with anhydrous diethyl ether and dried in an electric oven. (Yield 65–70%).

RESULTS AND DISCUSSION

The IR spectra of the ligands MPFS/MPFTS as well as their metal complexes are recorded in the region 4000–300 cm^{-1} and the results are shown in Table-2.

Semicarbazone and thiosemicarbazone ligands can coordinate with metal ions through carbonyl oxygen or thione sulphur and azomethine N-atom of either semicarbazone/thiosemicarbazone moiety[19]. The IR spectra of the ligands MPFS and MPFTS observed strong and broad band in the 3500–3400 cm^{-1} region which can be assigned ν(N—H) of secondary amino group of pyrimidine ring[20–22]. This band is shifted towards lower wavenumbers by 40–30 cm^{-1} in the complexation. This shifting indicates coordination may take place through secondary amino group of pyridine ring. The IR spectra of the ligand MPFS exhibit two more bands at 1760 and 1680 cm^{-1} which may be assigned to ν(C=O)[20–25] and ν(C=N)[20–25] respectively. Both the above mentioned bands go in red shift after complexation with ligand MPFS. This indicates the coordination may take place through carbonyl oxygen atom and azomethine N atom of semicarbazone moiety. The infrared spectra of the ligands MPFTS exhibit two strong and broad bands at 1660 cm^{-1} and at 820 cm^{-1} which may be assigned to $\nu(C{=}N)^{20-25}$ and $\nu(C{=}S)^{20-25}$ respectively. These bands after complex formation go into red shift which indicates coordination may take place through azomethine N-atom as well thione sulphur atom of thiosemicarbazone moiety. The coordinations through azomethine N-atom and oxygen/sulphur atom of either semicarbazone or thiosemicarbazone moiety are further confirmed by the occurrence of three bands in the far infrared regions at 580–540, 480–440 and 415–375 cm^{-1} which are assigned to $\nu(M{-}C)^{25,26}$, $\nu(M{-}S)^{25,27}$ and $\nu(M{-}N)^{25,28}$, respectively.

TABLE-2
IR SPECTRAL BANDS cm^{-1} OF LIGANDS MPFS/MPFTS AND ITS METAL COMPLEXES

Ligands/Complexes	$\nu(N{-}H)$	$\nu(C{=}O)$	$\nu(C{=}N)$	$\nu(C{=}S)$	$\nu(M{-}O)$	$\nu(M{-}S)$	$\nu(M{-}N)$
MPFS	3460 s, b	1760 s, b	1680 s, b	—	—	—	—
MPFTS	3420 s, b	—	1660 s, b	820 s, b	—	—	—
$[Co(MPFS)_2]Cl_2$	3430 m, b	1735 m, b	1650 m, b	—	580 m	—	380 m
$[Co(MPFTS)_2]Cl_2$	3395 m, b	—	1620 m, b	785 m, b	—	450 m	375 m
$[Co(MPFS)_2]Br_2$	3435 m, b	1730 m, b	1645 m, b	—	560 m	—	380 m
$[Co(MPFTS)_2]Br_2$	3390 m, b	—	1625 m, b	790 m, b	—	440 m	360 m
$[Co(MPFS)_2]I_2$	3425 m, b	1735 m, b	1655 m, b	—	540 m	—	365 m
$[Co(MPFTS)_2]I_2$	3385 m, b	—	1630 m, b	780 m, b	—	455 m	385 m
$[Ni(MPFS)_2]Cl_2$	3430 m, b	1730 m, b	1640 m, b	—	575 m	—	350 m
$[Ni(MPFTS)_2]Cl_2$	3380 m, b	—	1635 m, b	790 m, b	—	460 m	400 m
$[Ni(MPFS)_2]Br_2$	3420 m, b	1725 m, b	1645 m, b	—	555 m	—	395 m
$[Ni(MPFTS)_2]Br_2$	3390 m, b	—	1630 m, b	795 m, b	—	470 m	410 m
$[Ni(MPFS)_2]I_2$	3430 m, b	1720 m, b	1650 m, b	—	525 m	—	415 m
$[Ni(MPFTS)_2]I_2$	3395 m, b	—	1635 m, b	780 m, b	—	480 m	390 m
$[Cu(MPFS)_2]Cl_2$	3420 m, b	1735 m, b	1655 m, b	—	570 m	—	395 m
$[Cu(MPFTS)_2]Cl_2$	3390 m, b	—	1630 m, b	790 m, b	—	465 m	400 m
$[Cu(MPFS)_2]Br_2$	3425 m, b	1720 m, b	1650 m, b	—	560 m	—	410 m
$[Cu(MPFTS)_2]Br_2$	3380 m, b	—	1625 m, b	780 m, b	—	475 m	415 m

The electronic spectra of all the Co(II) complexes exhibit three spectral bands in the regions 8800–8300, 12800–12300, 20600–20000 cm^{-1} which may be assigned to the transitions, ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4A_{2g}(F)$, ${}^4T_{1g}(P)$ which indicate an octahedral[29–30] geometry of Co(II) complexes. The proposed geometry are further confirmed[31, 32] by high μ_{eff} value in the range 4.72–5.18 B.M. for all the Co(II) complexes. The Ni(II) complexes exhibit three absorption bands in the regions, 11700–11200, 17200–16400 and 23300–22600 cm^{-1} corresponds to $^4A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3T_{1g}(F)$, $^3T_{1g}(P)$ levels respectively which correspond to that of octahedral[30, 33] complexes. The proposed geometry of Ni(II) complexes further confirmed[31, 32] by the μ_{eff} values in the range 3.21–3.36 B.M. for all the Ni(II) complexes. The electronic spectra of all the Cu(II) complexes exhibit bands at 16300–15100 and 27300–26400 cm^{-1} which may be assigned to the transition $^4E_g \rightarrow {}^2T_{2g}$ and charge transfer bands. The electronic spectra for all the Cu(II) complexes suggest an octahedral[30, 34] geometry around Cu(II) complexes. The proposed geometry of all the Cu(II) complexes further confirmed[31, 32] by the μ_{eff} values in the range 1.86–1.97 B.M. for all the complexes.

Conductivities of the complexes of the type $[M(MPFS)_2]X_2$ and $[M(MPFTS)_2]X_2$ were measured in the solvent dimethyl formamide and all the complexes were found to be electrolytic[35] in nature of 1 : 2 type and molar conductivity values are in the range 95–127 ohm^{-1} cm^2 mol^{-1}.

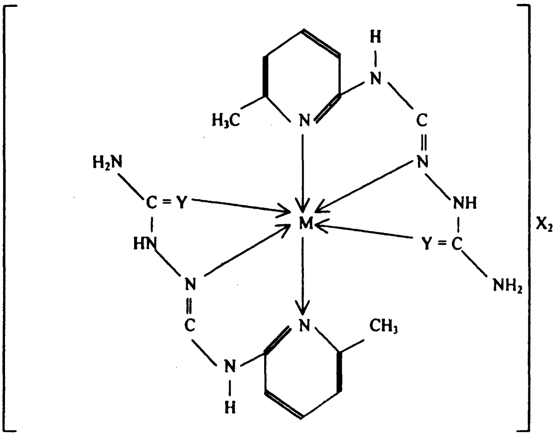
Antifungal activities of ligands MPFS and MPFTS as well as their metal complexes were carried out against *Aspergillus flavus* and *Aspergillus niger* by filter paper disc diffusion plate method[36]. The minimum inhibitory concentration (MIC) values in molar concentration ($\times 10^{-4}$) of the ligand and its metal complexes have been represented in Table-3. The data indicate that the metal complexes are more potent in inhibiting the growth of micro-organisms than the ligands.

TABLE-3
MINIMUM INHIBITORY CONCENTRATION (MIC) VALUES OF FUNGICIDAL GROWTH IN MOLAR CONCENTRATION ($\times 10^{-4}$) OF THE LIGAND MPFS/MPFTS AND ITS METAL COMPLEXES

Compounds	*Aspergillus flavus*	*Aspergillus niger*
MPFS	0.136	0.131
MPFTS	0.189	0.192
$[Co(MPFS)_2]Cl_2$	0.212	0.216
$[Co(MPFTS)_2]Cl_2$	0.224	0.236
$[Ni(MPFS)_2]Cl_2$	0.240	0.238
$[Ni(MPFTS)_2]Cl_2$	0.241	0.237
$[Cu(MPFS)_2]Cl_2$	0.247	0.244
$[Cu(MPFTS)_2]Cl_2$	0.251	0.256

The enhanced antimicrobial activity of the metal complexes over their corresponding chelating agents may conveniently be explained by exploiting chelation theory[37]. Chelation reduces the polarity of the metal ion mainly because of the partial sharing of its positive charge with the donor groups and possible π-electron delocalization over the whole chelate ring. Since the plasma membrane in general is more permeable to non-polar compounds than to polar compounds, it is natural to hypothesize that the more lipoid-soluble compounds are more toxic simply because they enter the cell more rapidly[38].

Hence on the basis of elemental analysis, IR electronic spectra, magnetic susceptibility and molar conductance value, the complexes of Co(II), Ni(II) and Cu(II) have stoichiometry of the type $[M(MPFS)_2]X_2$ and $[M(MPFTS)_2]X_2$ can be presumed to have octahedral geometry as shown in Fig. 1.



$[M(MPFS)_2]X_2$ and $[M(MPFTS)_2]X_2$

$X = Cl^-$, Br^- or I^-; M = Co(II), Ni(II) or Cu(II); Y = oxygen or sulphur

Fig. 1

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