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Spectral, Magnetic and Antimicrobial Studies of Co(II), Ni(II) and Cu(II) Complexes with Bidentate Schiff Base Ligands

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ABSTRACT

The divalent metal complexes of cobalt, nickel and copper have been prepared with bidentate Schiff base derived by condensing 6-methyl-2-phenyl (4H) chromen-4-one and semicarbazide hydrochloride. The complexes obtained were characterized on the basis of their elemental analysis, I.R., electronic spectra, magnetic susceptibility, molar conductance data. The IR spectral data revealed that Schiff base, 6-methyl-2-phenyl (4H) chromen-4-semicarbazone (MPCS) behave as bidentate ligands and coordinated to Co(II), Ni(II) and Cu(II) via azomethine nitrogen and carbonyl oxygen of semicarbazone moiety of the ligand. MPCS and remaining coordination centre of metal ion are satisfied by anions such as Cl^-, Br^-, I^- and NO_3^-. On the basis of molar conductance data complexes are proposed non-electrolytic in nature. On the basis of physicochemical and spectroscopic studies, the structure of the Co(II), Ni(II) and Cu(II) complexes was proposed octahedral in nature. All the synthesized ligand and complexes have been screened for antimicrobial activity.

Key words: Co(II), Ni(II) and Cu(II)/ Schiff base/ MPCS/ Antimicrobial study.

INTRODUCTION

Prevention of disease by the development of active treatments that control illness with minimum side effect to the human being has become the vital goal of modern health care. The use of antibiotics in medicine has resulted in an increasing number of resistant strains of microorganism, through mutation and gene transfer. Medical research has proved through extensive evidence that most of the diseases are mainly caused by a breakdown in our body's key defence systems that protect the body with the help of cells of vital force of the body present in living organism. Actually during illness body protection is possible from the ravages of free radicals. From the literature survey it is reported[1,2] that free radicals contribute to more than 100 disorders in human including atherosclerosis, arthritis, CNS injury, cancer and AIDS. Free radicals due to environmental pollutants, radiation, chemicals, toxins, deep fried and spicy food and fast food as well as physical and mental strains due to heavy workload causes depletion of immune system, change in gene expression and induce abnormal proteins. Due to depletion of immune system natural antioxidants in different maladies, consuming antioxidants as free radical may be necessary[3-5].

The antioxidant activity of several plant materials have been recently reported by several workers. Many common plants have been evaluated for their antioxidant activities. These plants have been documented to be rich in chromen derivatives.

The above mentioned alarming situation and accelerating rate of resistance is creating life threatening condition for society by increasing of drug resistant microorganism and new emerging diseases coupled with the toxicity and unavailability of alternative non toxic medicine, which may be Schiff base compounds with improved properties and extended antibacterial spectrum towards the future resistant strains[6-10]. The study of these new Schiff bases provide the basis for developing functional models as antimalarial, antifungal, antiviral, anticancer and antibacterial properties. Literature survey indicate the biocidal activity of Schiff bases is increased many folds on coordination with suitable metal ion[11-12]. Keeping the above facts in mind and in continuation of of our earlier recent work[13-17] in this field, synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes with Schiff base ligand 6-methyl-2-phenyl (4H) chromen-4-semicarbazone are reported herein. The antimicrobial activity of the ligand and their complexes have been tested against two bacteria, *S. aureus* and *E. coli* and two fungi *A. niger* and *A. flavus*.

EXPERIMENTAL

All the reagents and solvents used were of analytical grade and used as received. Metal salts were obtained from B.D.H.

Preparation of ligand [MPCS]

A suspension of 6-methyl-2-phenyl (4H) chromen-4-one (2.36g; 0.01 m) in ethanol (20 ml) was treated with semicarbazone hydrochloride (1.2g, 0.01 m) dissolved in 10% alcoholic solution of sodium acetate. The resulting reaction mixture was heated on water bath for 3 and half hour when a crystalline colourless solid began to separate. It was heated for further half an hour for complete precipitation. It was cooled, filtered, washed with aqueous ethanol, dried and crystallized with methyl alcohol as colourless solid was obtained. m.p.-232°C. It was analysed as $C_{12}H_{15}N_3O_2$.

Preparation of the complexes

All the Schiff base complexes were prepared by adding stoichiometric amount of ligand MPCS to respective metal chloride/ nitrate in 2:1 mole ratio. To an ethanolic solution of 0.002 mole of Schiff base (MPCS), ethanolic solution of respective metal chloride/ metal nitrate (0.001 mol) were added. The reaction mixture was refluxed for about 4-5 h. The pH was adjusted to optimum level. The complexes which precipitated were filtered off, washed with cold ethanol and recrystallized from ethanol. The products were finally dried in vacuum over fused calcium chloride.

RESULTS AND DISCUSSION

Melting points were determined in open capillaries and are uncorrected. I.R. spectra (KBr) were recorded on a Perkin-Elmer 577 grating I.R. spectrometer in the range 4000-200 cm ^{1}. The conductivity measurements were made on Systronics conductometer model 303 using D.M.F. as a solvent. The electronic spectra in DMF were recorded on a Cary 2390 spectrophotometer. Magnetic moments were measured by Gouy method using $Hg[Co(NCS)_4]$ as a calibrant. The ligand as well as metal complexes were analysed using standard[16] methods.

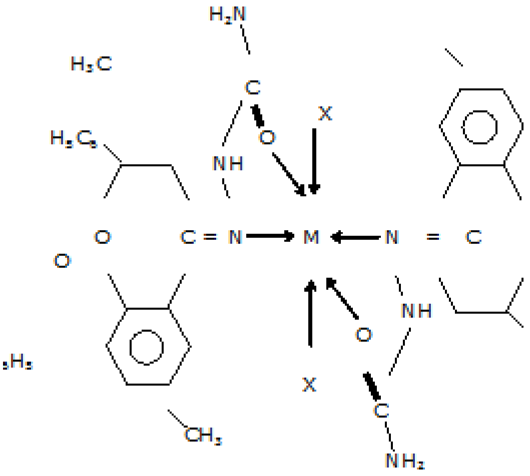
Infrared Spectra

The characteristic IR bands (4000-200 cm^{-1}) for the free ligand MPCS when compared with those of its Co(II), Ni(II) and Cu(II) complexes provided meaningful informations regarding the bonding sites of the ligand.

It is established[19-20] that semicarbazone ligand can coordinate through azomethine nitrogen and carbonyl oxygen atoms of semicrabazone. The ir spectrum of the ligand MPCS exhibits sharp and strong band at 1660 cm^{-1} which can be assigned[19-21] to $n_{C=O}$. The bond is shifted to higher wave numbers on complexation which indicates co-ordination to take place through carbonyl oxygen atom of semicrabazone moiety. It is further supported by the appearance of new band at 525-495 cm^{-1} in the complexes assignable[19-21-24] to $\nu_{M–O}$.

The next I.R. band of structural significance in the spectra of the ligands MPCS appears at 1475 cm^{-1}. It can be assigned[19-27] to $\nu_{C=N}$. In the spectra of the complexes this band suffered a downward shift of 20-30 cm^{1} and clearly indicates the coordination of azomethine N to the metal ion which is further supported by the appearance of a new band at 430-390 cm^{-1} in the complexes which may be assignable to $\nu_{M–N}$[19-21-24].

The coordination through halogen atoms are confirmed by the appearance of a band in the far infrared region between 325-255 cm^{-1}, which may be assigned to $\nu_{M–X}$[19-21-24] (X = $Cl^–$, $Br^–$ or $I^–$). The evidence of metal halogen linkage is further confirmed on the basis of low value of molar conductance of the complexes in the range 16.7-28.5 ohm^{-1} cm^{2} mol^{-1}. The presence of two bands at 1700 cm^{-1} and 1580 cm^{1} with a separation of 120 cm^{-1} suggests mono-coordinated nature of nitrate group[28-29].



MPCS = 6-methyl-2-phenyl (4H) chromen-4-semicarbazone

M = Co(II) and Ni(II); X = Cl^-, Br^-, I^- and NO_3^-; M = Cu(II); X = Cl^-, Br^- and NO_3^-

Fig.1: $[M(MPCS)_2]X_2$

Thus on the basis of physiochemical and infrared spectral data it is proposes that the MPCS acts in a bidentate ligand and coordination is proposed through azomethine N and oxygen atom of semicarbazone moiety. The remaining coordination centers of the metal ions are satisfied by the negative ions such as $Cl^–$, $Br^–$, $I^–$ and $NO_3^–$.

Electronic spectra and magnetic susceptibility of the complexes

The electronic spectra of all the complexes have been recorded in the region 10,000-25,000 cm^{-1}. The cobalt complexes exhibits three spectra bands in the region, 9000-10000 cm^{-1}, 13700-14300 cm^{-1} and 19300-20000 cm^{-1} assigned to $^4T_{2g}$ (F) ← $^4T_{1g}$(F), $^4A_{2g}$ (F) ← $^4T_{1g}$ (F) and $^4T_{1g}$ (P) ← $^4T_{1g}$ (F) respectively. The above mentioned spectral bands indicate octahedral[28-29] geometry for the Co(II) complexes. The octahedral geometry of Co(II) complexes is also supported[30-31] by magnetic susceptibility value in the range 4.92-5.21 B.M. The Ni(II) complexes exhibit three absorption bands in the region 11900-13000 cm^{-1}, 18200-19300 cm^{-1} and 24900-25900 cm^{-1} assigned to $^3T_{2g}$ (F) ← $^3A_{2g}$ (F), $^3T_{1g}$ (F) ← $^3A_{2g}$ (F) and $^3T_{1g}$ (P) ← $^3T_{2g}$ (F) transitions respectively. The above absorption bands of Ni(II) complexes suggesting octahedral[31-34] geometry which further supported[32-33] by magnetic susceptibility values of the complexes lie in the range 3.17-3.22 B.M.. The Cu(II) complexes display two ligand field bands in the regions, 12900-13300 cm^{-1} and 17700-18500 cm^{-1} assigned to $^2T_{2g}$ (F) ← ^2E_g and charge transfer band respectively which proposes octahedral geometry[31-35] for Cu(II) complexes. The magnetic susceptibility value of Cu(II) complexes lie in the range 1.89-1.93 B.M..

Molar conductance measurement of the complexes of Co(II), Ni(II) and Cu(II) were found to be in the range 2.6-6.9 ohm^{-1} cm^{2} mol^{-1} in DMF indicating their non electrolytic[36] nature. The molar conductance also support the structure assigned on the basis of physicochemical and spectroscopic measurements.

Antimicrobial activity

Ligand MPCS and their metal complexes were assayed in vitro for their ability to inhibit the growth of representative Gram positive (*Staphylococcus aureus*) and Gram negative (*Escherichia coli*) bacteria and the

Table 1: Elemental analysis, Colour, Molar mass, Molar conductance, Magnetic susceptibility, Decomposition temperature and electronic spectra of ligand mpcs and its metal complexes

Compounds (Colour)	Yield (in %)	Mol. wt.	% Analysis found (calculated M	 C	 N	 H	Ω_m ohm^{-1}cm^{2}mol^{-1}		DT°C	μ_{eff}B.M	λ_{max} electronic cm^{-1}
MPCS (Colourless)	65	231		69.39 (69.62)	14.21 (14.33)	5.04 (5.11)					
Co(MPCS)$_2$Cl$_2$] Brown	66	715.93	8.17 (8.23)	56.00 (56.98)	11.65 (11.73)	4.13 (4.19)	4.3	267	4.92		9000, 13900, 19300
[Co(MPCS)$_2$Br$_2$] Reddish brown	63	804.74	7.26 (7.32)	50.47 (50.69)	10.35 (10.43)	3.65 (3.72)	4.9	756	4.9		910000, 14300, 20000
[Co(MPCS)$_2$I$_2$]	60	898.74	6.42 (6.55)	45.26 (45.39)	9.22 (9.34)	3.27 (3.33)	5.2	284	5.21		9600, 14000, 19400
Green											
[Co(MPCS)$_2$(N O$_3$)$_2$] Light green	63	768.93	7.54 (7.66)	52.87 (53.06)	10.81 (10.92)	3.82 (3.90)	4.8	255	4.97		9500, 13700, 19900
[Ni(MPCS)$_2$Cl$_2$] Yellowish brown	67	715.71	8.12 (8.20)	56.81 (57.00)	11.62 (11.73)	4.11 (4.19)	5.7	281	3.17		12200, 18500, 25900
[Ni(MPCS)$_2$Br$_2$] Yellowish brown	70	804.52	7.10 (7.29)	50.56 (50.71)	10.32 (10.44)	3.64 (3.72)	6.2	273	3.20		11900, 18200, 24900
[Ni(MPCS)$_2$I$_2$]	60	898.52	6.46 (6.53)	45.23 (45.40)	9.23 (9.34)	3.27 (3.33)	6.9	294	3.71		13000, 19300, 25600
Yellowsih red											
[Ni(MPCS)$_2$(NO $_3$)$_2$] Brown	64	768.72	7.54 (7.63)	52.89 (53.07)	10.80 (10.92)	3.83 (3.90)	6.5	264	3.22		12600, 18600, 25400
[Cu(MPCS)$_2$Cl$_2$] Light bluw	68	720.54	8.74 (8.81)	56.49 (56.62)	11.58 (11.65)	8.74 (8.81)	3.4	297	1.90		13300, 18400
[Cu(MPCS)$_2$Br$_2$] Green	70	809.35	7.78 (7.85)	44.11 (44.25)	10.28 (10.37)	7.78 (7.85)	2.9	304	1.93		12900, 17700
[Cu(MPCS)$_2$(N O$_3$)$_2$] Green	69	773.54	8.14 (5.21)	52.69 (52.74)	10.76 (10.85)	8.14 (8.20)	2.6	309	1.89		13200, 18500

DT = Decomposition Temperature

Table 2: Key ir spectral bands (cm^{-1}) of ligand mpcs and its metal complexes

Compounds	$\nu_{C=O}$	$\nu_{C=N}$	ν_{M-O}	ν_{M-N}	ν_{M-X}
MPCS	1660 s,b	1475 s,m			
$[Co(MPCS)_2Cl_2]$	1690 m,b	1455 m,b	505 m	410 m	305 m
$[Co(MPCS)_2Br_2]$	1695 m,b	1455 m,b	510 m	415 m	280 m
$[Co(MPCS)_2I_2]$	1690 m,b	1450 m,b	505 m	420 m	270 m
$[Co(MPCS)_2(NO_3)_2]$	1685 m,b	1450 m,b	505 m	410 m	
$[Ni(MPCS)_2Cl_2]$	1690 m,b	1445 m,b	515 m	405 m,b	325 m
$[Ni(MPCS)_2Br_2]$	1685 m,b	1450 m,b	510 m	410 m	295 m
$[Ni(MPCS)_2I_2]$	1690 m,b	1455 m,b	500 m	415 m	275 m
$[Ni(MPCS)_2(NO_3)_2]$	1685 m,b	1455 m,b	500 m	420 m	
$[Cu(MPCS)_2Cl_2]$	1690 m,b	1450 m,b	490 m	410 m	315 m
$[Cu(MPCS)_2Br_2]$	1685 m,b	1460 m,b	490 m	410 m	285 m
$[Cu(MPCS)_2(NO_3)_2]$	1690 m,b	1455 m,b	485 m	410 m	

s,s = sharp and strong; m = medium, s = strong, b = broad

Table 3: The in vitro antimicrobial activities of ligand mpcs and their metal complexes

No.	Compound	Diameter of zone			
		C. albicans	*A. fumigatus*	*S. aureus*	*E. coli*
1	MPCS	12	08	07	09
2	$[Co(MPCS)_2Cl_2]$	22	16	04	10
3	$[Co(MPCS)_2I_2]$	20	13	05	08
4	$[Ni(MPCS)_2I_2]$	18	11		
5	$[Cu(MPCS)_2Cl_2]$	14	09	06	05
6	$[Co(MPCS)_2Br_2]$	12	07	08	09

fungus *Candida albicans* and *Aspergillus fumigatus*. The susceptibilities of certain strains of bacteria and fungus to the semicarbazone ligand and their complexes were evaluated by measuring the size of bacteriostatic diameter through paper disc plate method[37]. The results are given in Table 3. The result exhibits that the semicarbazone ligands are less active against the complexes due to chelation theory[38]. The data indicates antibacterial and antifungal activity of complexes were found to be in the order of Cu(II) > Ni(II) > Co(II).

CONCLUSION

Thus on the basis of above mentioned studies it is proposed that the complexes of Co(II), Ni(II) and Cu(II) are octahedral in geometry as shown in Fig. 1.

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