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Physico-Chemical and Antifungal Investigation of Co(II), Ni(II) and Cu(II) Complexes with Schiff Bases

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A new series of complexes of Co(II), Ni(II) and Cu(II) with 2-acetyl naphtho[2-1-b]furan semicarbazone (ANFS) have been synthesized and characterized by elemental analysis, conductivity, thermal analysis, magnetic moment, IR, UV-Vis spectral studies. From the analytical data the stoichiometry of the complexes has been found of the type $[M(ANFS)_2]X_2$, where X = Cl^-, Br^-, I^-, NO_3^- and ClO_4^-. IR spectral data suggest ligand coordinates to the metal ion through azomethine N, oxygen atom of furan ring of the ligand and carbonyl oxygen of semicarbazone. The high value of molar conductance suggests the complexes were found to be electrolytic in nature of 1:2 type. The physico-chemical data suggest that all the complexes possess octahedral geometry. The ligands as well as metal complexes are also screened for antifungal activity.

Key Words: 2-Acetyl naphtho[2-1-b]furan semicarbazone, Co(II), Ni(II) and Cu(II) complexes, Antifungal activity.

INTRODUCTION

The chemistry of Schiff base metal complexes is undergoing a rapid development and engaging the attention of researchers of many disciplines both experimental and theoretical. Studies of metal complexes with therapeutic compounds attains significant interest[1,2] due to its wide application in chemical, industrial, agricultural and biological field.

Recently, complexation has often been used to influence biological processes that are metal dependent[3,4]. At the same time many drugs behave as ligands coordinating to metals which affect their homoeostasis. It can be assumed therefore that the action of at least some of the drugs used in the treatment of metal dependent diseases can be explained on these grounds[5,6]. Arterial hypertension represents a good example of this type being sensitive to copper. In view of biological importance of Schiff base metal complexes and in continuation of our recent work[7-12] on the Schiff base metal complexes, we now describe the synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes with ligand 2-acetyl naphtho[2-1-b]furan semicarbazone (ANFS).

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EXPERIMENTAL

All the chemicals used were either E-Merck or BDH. 2-Acetyl naphtho[2-1,b]furan was synthesized by reported method[13]. Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer. The electronic spectra recorded on a Shimadzu 160A spectrophotometer. Molar conductance data were made on systronics conduc-tivity meter model 303 using DMF as a solvent. Magnetic susceptibility measured by a Guoy balance using mercury tetraisothiocyanato cobaltate as a calibrant. The metal contents were determined using standard procedures[14]. The analytical data, colour, magnetic susceptibility, conductivity value and electronic spectral data have been recorded in Table-1.

TABLE-1
ANALYTICAL, COLOUR, MAGNETIC MOMENT, CONDUCTIVITY VALUE, ELECTRONIC SPECTRA AND DECOMPOSITION TEMPERATURE OF LIGAND ANFS AND ITS METAL COMPLEXES

Compd. (colour)	Analysis found (calcd.)				μ_{eff} (BM)	Ω_m (ohm^{-1} cm^2 mol^{-1})	λ_{max} electronic (cm^{-1})	DT
	M	C	N	H				
ANFS	–	67.29	15.64	9.79	–	–	–	–
Cream		(67.41)	(15.73	(9.73)				
$[Co(ANFS)_2]Cl_2$	8.81	54.10	12.11	3.94	5.11	123.7	–	295
Green	(8.87)	(54.22)	(12.05)	(3.91)				
$[Co(ANFS)_2]Br_2$	7.77	47.73	11.09	3.49	5.04	120.7	13800	303
Yellowish Green	(7.82)	(7.82)	(11.15)	(13.45)			19200	
$[Co(ANFS)_2]I_2$	6.89	42.42	9.86	3.10	5.20	116.6	13800	301
Greenish Brown	(6.95)	(42.51)	(9.92)	(3.07)			19200	
$[Co(ANFS)_2](NO_3)_2$	8.26	50.30	11.65	8.26	4.95	121.4	12400	298
Green	(8.21)	(50.21)	(11.75)	(8.21)			19300	
$[Co(ANFS)_2](ClO_4)$	7.49	45.37	10.53	3.25	4.86	126.1	12600	303
Greenish Brown	(7.44)	(45.45)	(10.60)	(3.28)			19450	
$[Ni(ANFS)_2]Cl_2$	8.89	54.33	12.58	3.87	3.21	135.7	10000	312
Brown	(8.84)	(54.24)	(12.65)	(3.01)			15100	
							24100	
$[Ni(ANFS)_2]Br_2$	7.75	47.76	11.11	3.48	3.29	131.4	11000	314
Reddish Brown	(7.80)	(47.83)	(11.16)	(3.43)			15400	
							24000	
$[Ni(ANFS)_2]I_2$	6.97	42.61	9.97	3.02	3.41	132.7	10700	317
Reddish Brown	(6.93)	(42.52)	(9.90)	(3.07)			15500	
							24600	
$[Ni(ANFS)_2](NO_3)_2$	8.14	50.13	11.65	3.66	3.46	135.4	10800	293
Green	(8.19)	(50.22)	(11.72)	(3.62)			15900	
							24100	
$[Ni(ANFS)_2](ClO_4)$	7.47	45.34	10.65	3.33	3.56	133.3	10400	291
Light Green	(7.41)	(45.45)	(10.60)	(3.28)			16000	
							24700	
$[Cu(ANFS)_2]Cl_2$	9.54	53.72	12.50	3.92	1.71	114.3	11200	299
Green	(9.50)	(53.84)	(12.56)	(3.88)			14500	
$[Cu(ANFS)_2]Br_2$	8.33	47.62	11.14	3.39	1.80	112.1	11500	317
Brown	(8.38)	(47.53)	(11.09)	(3.43)			14600	
$[Cu(ANFS)_2](NO_3)_2$	8.73	49.78	11.58	3.56	1.76	110.3	11100	312
Deep Green	(8.80)	(49.89)	(11.64)	(3.60)			14400	
$[Cu(ANFS)_2](ClO_4)$	7.91	45.27	10.62	3.21	1.74	109.3	11500	308
Green	(7.97)	(45.19)	(10.54)	(3.26)			11800	

DT = Decomposition temperature.

Preparation of ligand/ANFS: A suspension of 2-acetyl naphtho[2-1,b]furan (2.10 g, 0.01 m) in ethanol (20 mL) was treated with semicarbazone hydrochloride (1.2 g, 0.01 m) dissolved in 10 % ethanolic solution of sodium acetate. The resulting reaction mixture were heated on water bath for 3 h when a crystalline colourless solid began to separate. It was heated for further 1 h for complete precipitation. It was cooled, filtered, washed with aqueous ethanol, dried and crystallized with methyl alcohol as cream colour solid. m.p. 232 ºC, yield 65-70 %.

Preparation of complexes: The complexes of Co(II), Ni(II) and Cu(II) have been isolated by reacting an ethanolic solution of respective metal salts with ethanolic solutions of the ligand ANFS in molar ratio 1:2. The resulting reaction mixture were heated on water bath for 3-4 h. The solid coloured complexes which separated out on cooling were filtered washed with ethanol dried and recrystallized with DMF. Yield 60-65 %.

RESULTS AND DISCUSSION

Infrared spectra: The IR spectra of the ligand ANFS exhibits a broad band of medium intensity at 3220 cm^{-1} which may be assigned[15] to ν(N-H). The spectra of the complexes exhibits this band without much change in position and intensity clearly indicating non involvement of nitrogen atom of either amino or imino group in the coordination with metal ion. The spectrum of the ligand ANFS also exhibits a sharp and strong band at 1690 cm^{-1} which can be assigned[16]16 to ν(C=O). In the spectra of the complexes, this band has shifted to a higher frequency region with slightly reduced intensity. The shift of the band and change in intensity suggest coordination of carbonyl oxygen group of semicarbazone moiety to the metal ion. The next IR band of structural significance in the spectra of the ligand ANFS, appears at 1475 cm^{-1} which can be assigned[17] to ν(C=N) group. This band also suffered downward shift by 20-30 cm^{-1} in the complexes indicating the coordination of the nitrogen to the metal ion.

The IR spectra of the ligand exhibit in the range of 1200-1000 cm^{-1} has been shifted towards the lower frequency side in all the complexes indicating the involvement of furan oxygen in the complex formation. The coordination of metal ions through azomethine nitrogen and oxygen atoms are further confirmed by the appearance of bands in the far infrared region 570-520, 395-360 cm^{-1} which may be assigned[18] to ν(M-O) and ν(M-N), respectively.

The electronic spectral and magnetic susceptibility data (Table-2) suggest octahedral geometry of the complexes.

Antifungal activity: The ligand ANFS and its complexes with Co(II), Ni(II) and Cu(II) have been screened for their antifungal activity against *A. niger* and *C. albicans* at concentrations at 25 and 50 mg mL^{-1} employing the paper disc plate method[19]. The minimum inhibitory concentration values are listed in Table-3.

Conductivity measurements: Conductivity of the complexes of the type $[M(ANFS)_2]X_2$ were measured in the solvent DMF and all the complexes were

TABLE-2
INFRARED SPECTRA DATA FOR LIGAND ANFS AND ITS METAL COMPLEXES

Compounds	ν(N–H)	ν(C=O)	ν(C=N)	ν(M–O)	ν(M–N)
ANFS	3220 m,b	1690 s,s	1475 s,b		
$[Co(ANFS)_2]Cl_2$	3220 m,b	1720 m,b	1440 m,b	550 m	375 m
$[Co(ANFS)_2]Br_2$	3220 m,b	1715 m,b	1450 m,b	530 m	380 m
$[Co(ANFS)_2]I_2$	3220 m,b	1710 m,b	1445 m,b	520 m	360 m
$[Co(ANFS)_2](NO_3)_2$	3220 m,b	1720 m,b	1450 m,b	530 m	370 m
$[Co(ANFS)_2](ClO_4)$	3220 m,b	1715 m,b	1445 m,b	540 m	395 m
$[Ni(ANFS)_2]Cl_2$	3220 m,b	1710 m,b	1450 m,b	535 m	370 m
$[Ni(ANFS)_2]Br_2$	3220 m,b	1720 m,b	1445 m,b	525 m	360 m
$[Ni(ANFS)_2]I_2$	3220 m,b	1715 m,b	1440 m,b	540 m	380 m
$[Ni(ANFS)_2](NO_3)_2$	3220 m,b	1710 m,b	1450 m,b	550 m	360 m
$[Ni(ANFS)_2](ClO_4)$	3220 m,b	1720 m,b	1445 m,b	545 m	365 m
$[Cu(ANFS)_2]Cl_2$	3220 m,b	1715 m,b	1450 m,b	570 m	370 m
$[Cu(ANFS)_2]Br_2$	3220 m,b	1710 m,b	1445 m,b	560 m	365 m
$[Cu(ANFS)_2](NO_3)_2$	3220 m,b	1710 m,b	1450 m,b	540 m	360 m
$[Cu(ANFS)_2](ClO_4)$	3220 m,b	1720 m,b	1440 m,b	520 m	380 m

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

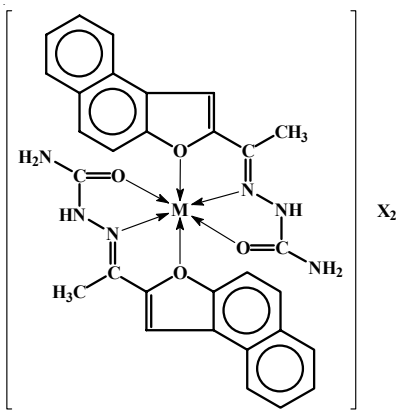
TABLE-3
ANTIFUNGAL ACTIVITY OF THE LIGAND ANFS AND
ITS METAL COMPLEXES OF Co(II), Ni(II) AND Cu(II)

Compounds	MIC (mg mL^{-1})	
	A. niger	*C. albicans*
ANFS	14	16
$[Co(ANFS)_2]Cl_2$	29	32
$[Co(ANFS)_2]Br_2$	31	36
$[Ni(ANFS)_2]Cl_2$	33	40
$[Ni(ANFS)_2]Br_2$	37	43
$[Cu(ANFS)_2]Cl_2$	42	54
$[Cu(ANFS)_2]Br_{2m}$	47	57

found to be electrolytic[20] in nature of 1:2 type and conductivity values are in the range 109.3-135.7 ohm^{-1} cm^2 mol^{-1}.

Conclusion

On the basis of elemental analysis, infrared spectra, electronic spectra, magnetic moment, thermal study and conductivity measurement data, the ligand ANFS acts in a neutral tridentate manner and coordination takes place through phenolic oxygen atom of furan ring, imine N atom and carbonyl oxygen of the semicarbazone moiety of the ligand. The geometry of the complexes were proposed to be octahedral in nature as shown in Fig. 1.



$[M(ANFS)_2]X_2$; M = Co(II), Ni(II) and Cu(II); X = Cl^-, Br^-, I^-, NO_3 and ClO_4^-

Fig. 1.

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