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Synthesis and Spectroscopic Studies of Metal Complexes of Schiff Base Derived From 2-acetyl naphtho [2,1-b] furan.

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ABSTRACT

A bidentate oxygen/ nitrogen containing Schiff base ligand 2-acetyl naptho [2,1-b] furan hydrazone (ANFH) and their Co(II), Ni(II) and Cu(II) complexes have been synthsized and characterized by molar mass, elemental analyses, spectroscopic (IR and electronic), molar conductivity and magnetic susceptibility measurements at the room temperature. On the basis of above studies it is proposes that ligand is suggested to acts in a bidentate manner and coordination proposes through azomethine nitrogen and nitrogen atom of furan ring. The remaining coordination centre are satisfied by negataive ions such as Cl^-, Br^-, I^- and NO_3^-. The Co(II), Ni(II) complexes have octahedral geometry where as Cu(II) complexes were proposed distorted octahedral geometry.

Keywords : ANFH/ Schiff base/ Co(II)/ Ni(II)/ Cu(II) complexes.

INTRODUCTION

The Schiff bases are the most versatile and thoroughly studied ligand in coordination chemistry. Metal complexes of Schiff bases have been reported as tuberculostatic, antitumor, antibacterial and antifungal agents. Transition metal complexes with Schiff base ligands have been prepared in view of their potential application as antibacterial and antifungal drugs. The importance of Schiff base ligands and their complexes with transition metal have enhanced especially due to their biological application. Metal chelates with multidentate Schiff base have been used for the purification of metals due to their high voltality and solvability in non polar solvent[1-2]. The metal complexes with Schiff bases find various industrial and biological applications. Schiff base metal complexes have scarcely been investigated[3-7]. The interest in the study of hydrazones possessing potential donor sites has been intensively increasing last years because of their ability to form stable chelates with transition metals present in the vivid cell[8,9]. This process inhibits many vital enzymatic reactions catalyzed by the metal ions. It has been also observed that the biocidal activity of the hydrazones increased by complexation to metal ions such as cobalt, nickel and copper. Thus a considerable metal complexes have been reported as antitumor[10-11], tuberculostatic[12,13], antifungal[14,15] agents. Thus the aim of present work is to synthesize and characterize Co(II), Ni(II) and Cu(II) complexes with Schiff base 2-acetyl naptho [2,1-b] furan hydrazone [ANFH].

Table-1:Analytical and physical measurements of ligand ANFH and its Co(II), Ni(II) and Cu(II) complexes

Compounds (Colour)	Molar mass	Yield %	% Analysis found (calculated)				μ_{eff} B.M.	Ω_m ohm^{-1} cm^2 mol^{-1}	DT ^oC	λ_{max} electronic cm^{-1}
			M	C	N	H				
ANFH	224	65		74.85	12.39	5.27				
(Colourless)				(75.00)	(12.50)	(5.35)				
[Co(ANFH)$_2$Cl$_2$]	577.93	67	10.08	58.01	9.60	4.09	4.89	1.9	231	13000, 17900 22900
(Brownish red)			(10.19)	(58.13)	(9.68)	(4.15)				
[Co(ANFH)$_2$Br$_2$]	666.74	66	8.77	50.24	8.30	3.52	4.92	1.7	236	13080, 18300 22700
(Brown)			(8.83)	(50.39)	(8.39)	(3.59)				
[Co(ANFH)$_2$I$_2$]	760.73	69	7.68	44.02	7.28	3.10	4.95	1.3	232	13200, 18100, 23100
(Brown)			(7.74)	(44.16)	(7.36)	(3.15)				
[Co(ANFH)$_2$(NO$_3$)$_2$]	630.93	70	9.27	53.11	8.79	3.74	4.97	0.9	220	12060, 18000 23300
(Dark brown)			(9.34)	(53.25)	(8.87)	(3.80)				
[Ni(ANFH)$_2$Cl$_2$]	577.71	70	10.07	58.02	9.60	4.09	3.17	1.8	190	12100, 17600 24060
(Green)			(10.16)	(58.16)	(9.69)	(4.15)				
[Ni(ANFH)$_2$Br$_2$]	666.52	70	8.71	50.28	8.32	3.53	3.11	2.1	198	12600, 17100, 24020
(Brownish green)			(18.80)	(50.41)	(8.40)	(3.60)				
[Ni(ANFH)$_2$I$_2$]	760.52	70	7.67	44.04	7.28	3.49	3.18	2.4	201	12300, 17300 24000
(Deep green)			(7.71)	(44.18)	(7.34)	(3.15)				
[Ni(ANFH)$_2$(NO$_3$)$_2$]	630.71	68	9.22	53.14	8.78	3.72	3.16	2.6	216	12400, 17400, 24100
(Greenish brown)			(9.30)	(53.27)	(8.87)	(3.80)				
[Cu(ANFH)$_2$Cl$_2$]	582.54	65	10.81	57.54	9.52	4.05	1.97	1.1	213	13300, 19200
(Blue)			(10.90)	(57.67)	(9.61)	(4.11)				
[Cu(ANFH)$_2$Br$_2$]	671.35	65	9.39	49.66	8.27	3.49	1.94	1.2	212	13600, 19800
(Blue)			(9.46)	(50.01)	(8.34)	(3.57)				
[Cu(ANFH)$_2$(NO$_3$)$_2$]	636.54	70	9.90	52.62	8.68	3.70	1.93	1.4	207	13200, 19100
(Deep blue)			(9.98)	(52.76)	(8.79)	(3.77)				

DT = Decomposition Temperature

Table 2: IR spectral band of the ligand ANFH and its complexes.

Compounds	$\nu_{c=n}$	ν_{Cm-o}	ν_{M-N}	ν_{M-X}
ANFH	1475, s,b			
$[Co(ANFH)_2Cl_2]$	1450 n	540 m	460 m	265 m
$[Co(ANFH)_2Br_2]$	1450 m	530 m	460 m	270 m
$[Co(ANFH)_2I_2]$	1455 m	520 m	460 m	275 m
$[Co(ANFH)_2(NO_3)_2]$	1455 m	510 m	465 m	280 m
$[Ni(ANFH)_2Cl_2]$	1450 m	525 m	470 m	305 m
$[Ni(ANFH)_2Br_2]$	1445 m	535 m	475 m	310 m
$[Ni(ANFH)_2I_2]$	1445 m	540 m	470 m	325 m
$[Cu(ANFH)_2Cl_2]$	1445 m	545 m	460 m	290 m
$[Cu(ANFH)_2Br_2]$	1445 m	545 m	480 m	295 m
$[Cu(ANFH)_2(NO_3)_2]$	1450 m	555 m	490 m	300 m

m = medium, s = strong, b = broad

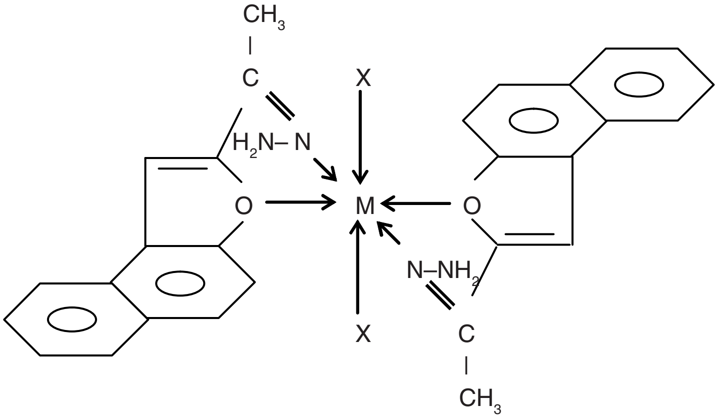

Fig.1

$[M(ANFH)_2 X_2]$

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

All the reagents used were of analytical reagent grade [A.R.]. The solvents were used without any purification. The metal contents were determined using standard procedure[16]. The analytical data, colour, magnetic susceptibility, molar conductance, electronic spectra, decomposition temperature are given in Table-1. The magnetic susceptibility were measured by Gouy method using $Hg[Co(NCS)_4]$ as a calibrant. Electronic spectra of the complexes were recorded in DMF on Cary-2300 spectrophotometer. The IR spectra of the ligand and metal complexes were recorded on Perkin-Elmer model-577 using KBr disc. Molar conductance of the complexes were recorded by Systronics conductivity meter model 303 in DMF.

Preparation of ligand (ANFH)

Schiff base (ANFH) was synthesized by the condensation of equimolar ratio of 2-acetyl naptho [2,1-b] furan and hydrazine hydrate dissolved in ethanol. The resulting mixture was stirred well, refluxed for 4-5 h and then allowed to cool overnight. The coloured solid precipitate of Schiff base obtained was filtered, washed with cold ethanol several times and dried in air at room temperature and finally recrystallized with tetrahydrofuran. Yield 65%; m.p.-207 ± 1°C.

Preparation of the complexes

The Co(II), Ni(II) and Cu(II) complexes were prepared by the treatment of ethanolic solution of 2-acetyl naptho [2,1-b] furan hydrazine (ANFH) (0.002m) with ethanolic solution of respective metal chlordie/ nitrate (0.001 m) and refluxed for 3-4 h. The complexes obtained were washed with water, ethanol and diethyl ether, dried in desiccator and stored in air tight bottles.

RESULTS AND DISCUSSION

The IR spectrum of the ligand exhibits a broad band at 1475 cm^{-1} assigned to $\nu_{(C=N)}$. This band shifts to lower wave number in complexes by 20-35 cm^{-1}, indicating participation of the azomethine nitrogen in bonding with metal ions. The coordination through azomethine N atom is further supported by the presence of metal-ligand vibration band in the far ir region at 490-460 cm^{-1} are assigned[18,19] to $n_{(M–O)}$. The next ir spectrum of the ligand exhibit in the range 1200-1000 cm^{-1} has shifted towards the lower frequency side in all complexes indicating the involvement of furan oxygen in the complex formation. The linkage with oxygen atom is further confirmed by the presence of a band in far IR region at 555-510 cm^{-1} assigned[18,19] to $\nu_{(M–O)}$.

The coordination through metal halogen is indicated by the appearance of a band in region 325-265 cm^{-1} asigned[18,19] to $\nu_{(M–X)}$ (X=Cl^-, Br^- or I^-). The evidence of metal halogen linkage is further confirmed by the low value of molar conductance in the range 0.9 to 2.6 ohm^{-1} cm^{2} mol^{-1}.

The presence of two band at 1670 and 1550 cm ^{1} with a separation of 120 cm^{-1} suggest mono coordinate linkage of nitrate group with metal ion.

Electronic spectra and magnetic susceptibility data of the complexes

The electronic spectra of Co(II) complexes show three bands in the region 12060-13200, 17900-18300 and 22700-23300 cm^{-1}. The above observation frequencies are assignable to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{2g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, transitions respectively in an octahedral[20] environment. The octahedral geometry for Co(II) complexes are further supported[21,22] by the high value of magnetic susceptibility in the range 4.89-4.97 BM. The Ni(II) complexes exhibit three absorption band 12000, 17000 and 24000 cm^{-1} assignable to $^3A_{2g}(F) \rightarrow {}^4T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^4T_{2g}(P)$ transitions respectively in an octahedral[20] environment. The proposed octahedral geometry of Ni(II) complexes supported[21,22] by the magnetic susceptibility value in the range 3.11-3.18 BM.

The Cu(II) complexes exhibit two spectral bands in the region 13200-13600 and 19800-19100 cm^{-1} assigned to $^2E_g \rightarrow {}^2T_{2g}$ and CT bands respectively which proposes octahedral[20] geometry. The magnetic susceptibility[21,22] value for Cu(II) complexes are found in the range 1.93-1.97 BM.

CONCLUSIONS

The synthesized Schiff base, ANFH acts as a neutral bidentate ligand. The metal ions are coordinated through azomethine N and oxygen of furan ring. The remaining coordinated centres are satisfied by negative ion such as Cl^-, Br^-, I^- or NO_3^-. Thus on the basis of above studies the geometry of Co(II) and Ni(II) complexes are proposed to octahedral where as geometry of Cu(II) complexes are distorted octahedral as shown in Fig.1.

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